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THE ABSORPTION OF ACID DYES

By Wool, Silk, Casein Fiber and Nylon*

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INTRODUCTION

THE absorption of acid dyes by wool has been the subject of extensive study in the past, as a result of which a fairly satisfactory general picture of the dyeing mechanism has evolved. There are, however, several detailed aspects of the dyeing process which are not fully understood and regarding which there is a lack of precise data. It was with the object of filling in some of these gaps that the present work was undertaken.

A particularly striking lacuna is that concerned with the effect of variations in the concentration of dye in the dyebath[1]. The effect of dyebath acidity on dye absorption has been studied in great detail, but the effect of dye concentration at constant acidity scarcely at all. This deficiency is all the more striking because isotherms showing the relationship between the concentration of dye in the bath and on the fiber are of particular value in studying the dyeing mechanism.

Early investigators (1900-1910) paid some attention to this aspect of dyeing, for it seemed to provide a simple method of deciding whether dyeing is taking place by adsorption or by chemical combination. Thus, Freundlich and Losev[2] investigated the dyeing of Crystal Ponceau and Patent Blue on wool, and compared this with the adsorption of the same dyes on charcoal. They were able to show that the process appeared to be the same in both cases and that the data could be fitted by the Freundlich adsorption isotherm. Similar results were obtained by Pelet-Jolivet[3], and it was concluded that the dyeing of wool was an adsorption process. Knecht[4], on the other hand, favored the formation of a wool-dye salt, and his absorption isotherm for Crystal Ponceau does not fit the Freundlich equation. A possible reason for the discrepancy is that Knecht covered a wider range of concentration than did the other workers and approached saturation of the wool fiber. This matter does not appear to have been pursued to a satisfactory conclusion and no further detailed investigation of the subject is recorded in the literature. The reason may be that evidence from other experiments provided more positive and conclusive proof of the salt-formation theory of wool dyeing, so that interest in the adsorption isotherm lapsed. Yet the subject is still one of considerable theoretical and practical interest, and it was thought worth while to carry out absorption experiments covering a wide range of concentration up to saturation of the fiber.

At the same time the opportunity was taken to extend the investigation to fibers other than wool, and accordingly absorption isotherms on silk, casein fiber and nylon have also been determined. Because of their recent introduction, the last two fibers have not previously been subjected to the same detailed investigation as have wool and silk, and it was thought that a comparison of the absorption properties of the four fibers would prove very illuminating.

A third objective in this work was to compare the behavior of a typical level dyeing acid dye with that of an acid dye of the "milling" type. Nearly all the published quantitative data on the dyeing of wool refer to the simple azo dyes which are crystalloidal in solution and have little or no affinity for wool from neutral solutions. Only in one or two cases, notably the work of Goodall[5], have "colloidal" dyes of high wet-fastness and good neutral dyeing properties been investigated. The work described in the present paper still does not adequately fill this gap in our knowledge, but we have at least investigated the behavior of one acid dye of the milling type in some detail.

Before proceeding to describe the experimental work, it seems desirable to outline briefly the modern theory of the wool dyeing process, as visualized by the present authors, in order to provide a basis for discussion and an indication of the points regarding which more information is desirable.

The work of Astbury,[6] Speakman and others has established conclusively that wool is built up of amino-acids condensed in long polypeptide chains of the type—

$$\text{—CH.CO.NH.CH.CO.NH.CH—}$$
$$\quad\quad\quad

must take place in the amorphous intermicellar material. This results in a moving apart of the micelles to a point at which osmotic pressure is balanced by elastic forces tending to restore the fiber to its original state. In this swollen condition the intermicellar material forms open networks or pores between the crystallites. The diameter of these pores is not known with certainty, but is probably about 60A in wool. In any case, it seems probable that the pores are sufficiently large to permit of the passage of dye molecules.

If the cross-section of a normal dyed fiber is examined, it is seen to be uniformly colored. The dye has penetrated to the center and, since it cannot have passed through the crystalline portions, which are unswollen, it must have diffused along the intermicellar pores. In other words, on placing the fiber in the dyebath, swelling takes place, resulting in pores along which dye can diffuse. Once inside the fiber, the dye must be fixed in some way in order to account for the progressive increase in exhaustion of the dyebath. It is at this point that the chemistry of the fiber becomes important.

The fixation of the dye is attributed to the amino- and carboxyl groups carried on the side-chains. In the neutral fiber an internal salt is formed by the transfer of a hydrogen ion from a carboxyl group to give a positively charged substituted ammonium ion and a negatively charged carboxyl ion. The electrostatic attraction between these two oppositely charged groups forms the so-called "salt-link," which helps to hold adjacent main chains together and thus plays an important part in the physical properties of the fiber. When placed in an acid solution, hydrogen ions diffuse rapidly into the fiber, entering, because of their small size, even into the unswollen crystalline portions and neutralizing the charges on the weakly acid carboxyl groups. Thus, the fiber is left with a positive charge and attracts any anions, e.g., sulfate or dye anions, which are present in the solution. These anions diffuse into the fiber through the pores and approach as closely as possible to the ionized amino-groups of the protein. In the main amorphous portion of the fibers the anions can approach very closely to the substituted ammonium groups, and chemically the process is equivalent to the formation of a salt between the dye-acid and the basic groups of the protein. Because of their size, however, dye anions are unable to penetrate the crystalline portions of the fiber, as may be shown by X-ray analysis, and it is possible that they collect on the surface of the micelles in numbers corresponding with the number of ionized groups inside the micelles. This is a point about which some uncertainty remains, for it has been argued[7] that the electrostatic forces which would be set up by such a separation of charged ions in the wool micelle would be so great as to render the system electrically unstable.

According to this theory of the dyeing of wool with acid dyes, the cause of dyeing is, in effect, the formation of a salt between wool and dye. This is supported by many experiments in which the maximum amount of acid which the wool fiber can absorb has been determined. Probably the acid-combining capacity has been determined most frequently and with greatest accuracy in the case of hydrochloric acid, and it has been shown that 1 g. wool will absorb 0.82 milliequivalent of hydrochloric acid. Numerous experiments with acid dyes have given saturation values corresponding fairly closely with this figure, so the evidence in favor of salt formation is very strong.

Certain difficulties, however, indicate that the mechanism cannot be quite as simple as is indicated in the preceding discussion. Thus, it has been stated that when wool is placed in an acid solution the hydrogen ions discharge the carboxyl ions and leave the positively charged amino-groups to exert their attraction upon the dye. However, when a wool fiber is placed in an alkaline solution, the reverse process must take place, the amino-groups being discharged by hydroxyl ions from the solution. The fiber will then be negatively charged and will repel dye anions, so that the forces which were initially effective in attracting dye to the fiber are reversed in alkaline solutions. Thus, if the formation of a dye-wool salt is the only factor involved in dyeing, then it must be anticipated that the dye will have a much smaller affinity in an alkaline solution. The experimental facts, however, are that, under these conditions, many dyes remain firmly fixed to the fiber, a fact which is not readily explained by the simple theory of dyeing already outlined. It is true that other dyes bleed off almost completely in alkaline solutions, but this does not affect the general argument.

A further difficulty is that if wool is placed in a neutral solution, or a solution at the isoelectric point of the wool fiber, then all the amino-groups in the wool will be satisfied by the corresponding carboxyl groups in the fiber, and it is difficult to see why any attraction for dye anions should be present, yet the fact remains that many dyes can be applied to wool from a neutral or even slightly alkaline dyebath.

Finally, it is difficult to explain on the simple dyeing theory the levelling effect of inorganic salts, e.g., sodium chloride or sodium sulfate. Elod[8] has shown conclusively that, during the dyeing process, a protein salt is first formed by the attraction of the protons and anions of the mineral acid in the dyebath to the wool molecules. Subsequently, the more slowly diffusing dye anions are absorbed by the fiber and, as this process takes place, a corresponding number of inorganic anions are liberated. It was hitherto difficult to understand why the small inorganic anions which had already attached themselves to the amino-groups of the fiber should be replaced by the dye anions.

In order to explain these facts, it has been suggested[1,9] that the dyes are attached to wool not only by ionic forces or salt links, but also by such forces as van der Waals forces, resonance forces and co-ordinate links, probably involving the chromophore and auxochrome groups. Evidence for the existence of such forces is found in the work of Pfeiffer,[10] who showed that simple dyes give well-characterized crystalline addition products with amino-acids. The forces involved will be of a type similar to those which are active in the dyeing of cotton, but will probably be stronger and will continue to be active even in alkaline solutions.

Additional evidence for this theory is provided by the work of Harris and his collaborators,[11] who measured the absorption of various acids, including a dye-acid, by wool over a range of pH values. When the amount of acid absorbed is plotted against pH, sigmoid curves are obtained, the absorption rising slowly at first with decreasing pH, then more rapidly and finally approaching a constant value. The curves for different acids are all of the same shape, but are displaced to a greater or less extent towards higher pH values as compared with the curve for hydrochloric acid. This displacement can only be explained on the assumption that the acid anions themselves possess a characteristic affinity for the wool fiber, and the general indications are that the larger and more complex the anion, the greater is its affinity for wool. This supports the view that hydrogen bonds and van der Waals forces are involved in the attachment of the anions to the fiber.

Another suggestion to account for the washing-fastness of many wool dyes is that the dyes cannot easily diffuse out of the fiber (at the low temperatures usually employed in washing), owing to the large size of their molecules as compared with the intermicellar pores. Further, aggregation of the dye may occur inside the fiber in a manner analogous to that which is known to occur in the soaping of azoic dyes and vat dyes on cotton. This again would improve the washing-fastness. It is quite possible that such mechanisms do play a part in the dyeing of some acid

dyes, and it should be noted that the forces tending to promote aggregation are the same as those (other than the salt links) which are supposed to attract dye to the fiber. Hence it may be difficult to resolve these two effects.

If the dye anion is capable of attaching itself to wool by linkages other than salt links, then in certain circumstances wool might absorb more dye than corresponds to a simple neutralization of amino-groups. Cases where this has occurred have been reported only on rare occasions in the literature.[3] In most cases, dye to the extent of 0.82 milliequivalent per g. wool has been absorbed,[4] which corresponds to the amount of hydrochloric acid absorbed, but this may well be due to the type of dyes used for these particular investigations. Nearly all workers have concentrated on simple azo dyes of the class usually known as level dyeing acid dyes. Now the difficulties which have just been enumerated, and for the explanation of which the additional forces must be brought in, are not exhibited to any great extent by dyes of this class. In the light of the above theory, it would appear that the level dyeing acid dyes depend almost entirely for their affinity for wool on the salt linkage, since they must be applied from dyebaths of low pH, are absorbed in quantities corresponding to the number of free amino-groups, and have poor washing-fastness. Acid dyes of the milling type, on the other hand, can be applied from neutral solution and are faster to washing.

After due consideration of this theory, it was thought that experiments along the lines already suggested might provide valuable information in many ways. Thus, the investigation of fibers having fewer free amino-groups and a smaller take-up of dye due to salt linkages might be expected to show more effectively the influence of other forces in dyeing. Further, highly oriented fibers such as silk might influence the aggregation of dye in the fiber. The isotherms themselves should provide some indication of the dyeing mechanism and, especially if dyeing is continued to saturation of the fiber, should indicate whether or not, in the case of an acid dye of the milling type, more dye has been absorbed than is required to saturate the basic groups in the fiber.

EXPERIMENTAL

In carrying out the experimental work needed to determine the isotherms, it was decided to use a fairly low pH value in the dyebath. The object of this was to ensure that all the amino-groups were liberated from the internal salt linkages, so that the saturation value of the fiber should be independent of the dissociation constant or affinity of the acid dye used. As already noted, the amount of dye absorbed at different pH values varies until the fiber is saturated, when it becomes reasonably constant. Since all the present work has been carried out with dyes which have a higher affinity than a simple mineral acid it may be anticipated that the use of pH values between 1 and 2 will ensure saturation of the fiber with dye.

The fibers used throughout this investigation were all in the form of yarn. The wool was 4/16 woolen yarn, the nylon was bright 43/17 3S yarn, the silk a spun-silk 2-fold 45 denier yarn, and the casein fiber a singles yarn having a count of 12.8 on the worsted system.

In the investigation first to be described, measurements were made of the absorption of Solway Blue BS (*Colour Index*, No. 1054) on wool, silk, casein fiber and nylon.

The fiber, in the form of yarn, was first scoured in 3% soap solution at 60° C. for 20 min. It was then rinsed, first in hot water and then in cold water, and finally allowed to condition for 2 days in the atmosphere of the laboratory. For each experiment 1 g. of fiber was weighed out and placed in a 500 c.c. flask fitted with a reflux air condenser. To the flask was added 400 c.c. of the dyeliquor. The latter was prepared by dissolving the necessary amount of dye in 300 c.c. of water, adding sufficient sulfuric acid to bring it to the correct pH (1.35 or 1.6), and making up to 400 c.c. with water. Experiments indicated that the pH value of the liquor was unchanged after dyeing. Dyeing was carried out at 85°C. for 6 hrs. This time was shown to be adequate for the attainment of equilibrium, except in the case of nylon, where equilibrium was more slowly established and it was found necessary to prolong dyeing for 15 hrs. After the required dyeing time, the fiber was separated by filtration through cotton wool, rinsed with cold water, dried and conditioned. A small portion of the dyed fiber, usually about 0.1 g., was extracted with 15 c.c. of 25% aqueous pyridine, with warming if necessary. This extraction was repeated. After diluting the combined extracts, the solution was examined colorimetrically against a standard solution of known dye content. From this, the concentration of dye on the fiber was calculated, the concentration of dye in the dyebath being estimated by difference. The nylon yarn dyeings, however, were estimated by dissolving a known weight of fiber in o-chlorophenol instead of by the pyridine extraction method. In some cases, where the total quantity of dye was small, its distribution was determined by measuring the strength of the exhaust dyeliquor and calculating the weight on the fiber by difference. The dyebath in these experiments contained only standard dye and sulfuric acid. By comparison with a sample of pure dye it was found that the standard contained 37% of dye and 63% of common salt.

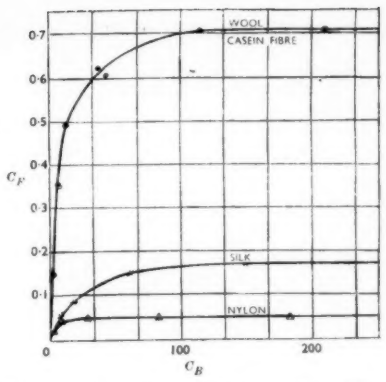

Fig. 1—Absorption of Solway Blue BS at pH 1.6.

C_F = Dye on Fiber in milliequivalent per g.

C_B = Residual Dye in Bath, in g.-equivalents per l.

Experiments were carried out in the first place at pH 1.35, but it was found that under these conditions silk was badly damaged, while casein fiber was slightly tendered. Hence, the isotherms were repeated at pH 1.6, which gave satisfactory results with all the fibers. Nevertheless, the isotherms of wool, casein fiber and nylon at pH 1.35 are recorded, since comparison of the results obtained at the two pH values is of interest. The full results are given in Tables I and II, illustrated by Figs. 1 and 2. The initial concentration of dye in the dyebath is expressed in g. of standard dye per l., the residual dye in g.-equivalents of pure dye per l. of liquor, and the dye on the fiber in milliequivalents of pure dye per g. of fiber.

TABLE I

Absorption Isotherms of Solway Blue BS on Wool, Silk, Casein Fiber and Nylon
pH 1.6; Temperature 85°C.; Dyeing time 6 hr. (15 hr. for nylon); and 1 g. of fiber in 400 c.c. of liquor

	Wool		*Casein Fiber*		*Silk*		*Nylon*	
Initial Concentration in Dyebath (g. standard dye per l.)	*Fiber (milliequivalent per g.)*	*Dyebath (g.-equivalents per l.)*	*Fiber (milliequivalent per g.)*	*Dyebath (g.-equivalents per l.)*	*Fiber (milliequivalent per g.)*	*Dyebath (g.-equivalents per l.)*	*Fiber (milliequivalent per g.)*	*Dyebath (g.-equivalents per l.)*
0.05	—	—	—	—	—	—	0.021	2.5×10^{-5}
0.125	—	—	—	—	0.042	9.0×10^{-5}	0.035	7.7×10^{-5}
0.25	0.148	2.3×10^{-5}	0.148	2.0×10^{-5}	0.081	18.7×10^{-5}	0.042	28.1×10^{-5}
0.625	0.365	6.25×10^{-5}	0.359	7.8×10^{-5}	0.145	60.9×10^{-5}	0.046	85.8×10^{-5}
0.875	0.491	14.0×10^{-5}	—	—	—	—	—	—
1.25	0.627	38.2×10^{-5}	0.605	43.7×10^{-5}	0.172	152×10^{-5}	0.049	183×10^{-5}
1.875	0.707	115×10^{-5}	—	—	—	—	—	—
2.50	0.710	212×10^{-5}	0.710	212×10^{-5}	0.176	346×10^{-5}	0.056	376×10^{-5}
5.0	0.718	602×10^{-5}	0.741	595×10^{-5}	0.184	735×10^{-5}	—	—

TABLE II

Absorption Isotherms of Solway Blue BS on Wool, Casein Fiber and Nylon
Details as in Table I, except that pH is 1.35

Initial Concentration in Dyebath (g. standard dye per l.)	Wool		Casein Fiber		Nylon	
	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)
0.5	—	—	—	—	0.009	5.6×10^{-6}
0.125	—	—	0.058	5.2×10^{-5}	0.021	14.5×10^{-6}
0.165	0.086	4.3×10^{-5}	—	—	—	—
0.25	—	—	—	—	0.030	31.6×10^{-6}
0.313	0.164	7.8×10^{-5}	—	—	—	—
0.625	0.328	15.6×10^{-5}	0.287	25.8×10^{-5}	0.041	87.5×10^{-6}
0.930	0.487	24.7×10^{-5}	—	—	—	—
1.25	0.625	39.0×10^{-6}	0.573	51.8×10^{-5}	0.056	181×10^{-5}
1.875	0.810	90.0×10^{-5}	—	—	—	—
2.5	0.875	172×10^{-6}	0.780	195×10^{-5}	0.071	373×10^{-5}
5.0	0.905	555×10^{-5}	0.90	556×10^{-6}	0.077	762×10^{-6}
7.5	0.935	937×10^{-5}	—	—	0.084	1150×10^{-6}

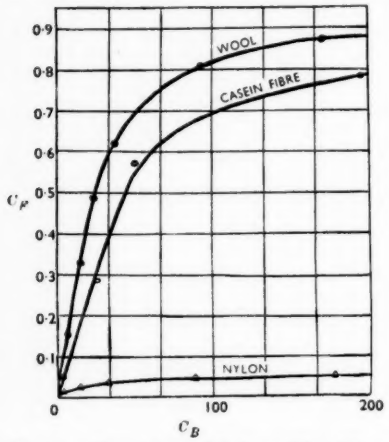

Fig. 2—Absorption of Solway Blue BS at pH 1.35.
C_F = Dye on Fiber in milliequivalent per g.
C_B = Residual Dye in Bath, in g.-equivalents per l.

In the remaining experiments to be described, the dyeing conditions were slightly different. The wool yarn was scoured in a solution containing 2 g. soap flakes and 0.5 c.c. 0.880 amounts per l. at 45° C. for 10 min. After rinsing, it was allowed to stand overnight in distilled water, squeezed, dried rapidly and conditioned. The nylon yarn was treated in a solution containing 3 g. soap and 1 c.c. 0.880 ammonia per l. at 60° C. for 20 min., rinsed hot and cold, dried and conditioned.

The dyeings were carried out on 2.5 g. of fiber in 250 c.c. of dyeliquor at 95° C. for 6 hr. The acidity was produced with sulfuric acid and was varied considerably in order to observe the effect of pH. The dyeliquor was examined colorimetrically after dyeing to determine the quantity of dye absorbed by the fiber.

In Table III the results of experiments using Carbolan Blue BS (I.C.I.) on wool at various dyebath pH values are recorded; the first column gives the initial concentration of dye in g. of standard dye per l., the standard containing 20 per cent of common salt, while the remaining concentrations are in milliequivalent of pure dye per g. of fiber and in g.-equivalents of pure dye per l. of liquor, as before. The results are illustrated in Fig. 3.

Two similar experiments were carried out on nylon with the results given in Table IV. The concentrations are expressed in the same form as before.

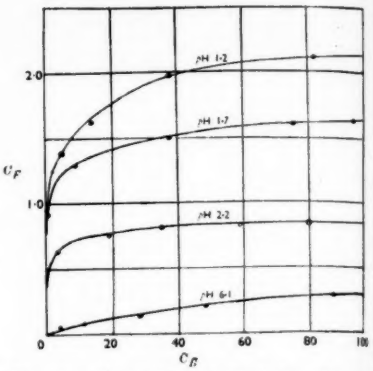

Fig. 3—Absorption of Carbolan Blue BS by Wool at various pH values
C_F = Dye on Fiber in milliequivalent per g.
C_B = Residual Dye in Bath, in g.-equivalents per l.

Dyeing experiments in neutral and acid solution were also carried out using Disulphine Blue V 250 (*Colour Index*, No. 712) containing 78 per cent dye and 22 per cent common salt. The preparation of the wool and dyeing conditions were exactly as described for Carbolan Blue BS, the only difference being due to the change in color which takes place with solutions of Disulphine Blue V at low

(Continued on Page 448)

TABLE IV

Absorption Isotherms of Carbolan Blue BS on Nylon at Different pH Values
Acid—Sulfuric acid; Temperature 95°C.; Dyeing time 6 hr.; and Liquor goods ration 100:1

Initial Concentration in Dyebath (g. standard dye per l.)	Dyebath pH 2.2		Dyebath pH 1.7	
	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)
0.1	0.023	very small	—	—
0.2	0.046	very small	—	—
0.3	0.069	very small	—	—
0.5	0.114	0.23×10^{-4}	—	—
7.5	0.149	2.56×10^{-4}	—	—
1.0	0.179	5.35×10^{-4}	0.120	2.33×10^{-4}
1.25	0.196	9.55×10^{-4}	—	—
1.5	0.202	14.7×10^{-4}	0.291	5.62×10^{-4}
2.0	0.233	23.3×10^{-4}	0.363	10.2×10^{-4}
2.5	0.256	32.6×10^{-4}	0.400	18.1×10^{-4}
3.0	0.256	44.3×10^{-4}	0.436	26.3×10^{-4}
4.0	—	—	0.442	40.0×10^{-4}
5.0	—	—	0.445	72.0×10^{-4}

TABLE III

Absorption Isotherms of Carbolan Blue BS on Wool at Different pH Values
Acid—Sulfuric acid; Temperature 95°C.; Dyeing time 6 hr.; and Liquor-goods ratio 100:1

Initial Concentration in Dyebath g. (standard dye per l.)	Dyebath pH 6.1		Dyebath pH 2.2		Dyebath pH 1.7		Dyebath pH 1.2	
	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)
0.5	0.063	5.0×10^{-4}	—	—	—	—	—	—
1.0	0.096	13.7×10^{-4}	0.225	0.81×10^{-4}	—	—	—	—
2.0	0.158	30.7×10^{-4}	0.450	1.63×10^{-4}	—	—	—	—
3.0	0.216	48.2×10^{-4}	0.653	4.65×10^{-4}	—	—	—	—
4.0	—	—	0.746	18.6×10^{-4}	0.92	0.93×10^{-4}	—	—
5.0	0.275	88.5×10^{-4}	0.816	34.9×10^{-4}	—	—	1.16	Very small
6.0	0.279	112×10^{-4}	0.816	58.2×10^{-4}	1.30	9.3×10^{-4}	1.37	2.33×10^{-4}
7.0	—	—	0.840	79.2×10^{-4}	—	—	—	—
7.5	—	—	—	—	—	—	1.61	14.0×10^{-4}
8.0	0.286	157×10^{-4}	—	—	1.49	57.3×10^{-4}	—	—
8.5	—	—	0.851	113×10^{-4}	—	—	—	—
10.0	0.291	204×10^{-4}	0.862	147×10^{-4}	1.58	74.6×10^{-4}	1.96	37.3×10^{-4}
12.0	—	—	—	—	1.61	95.5×10^{-4}	—	—
12.5	0.293	262×10^{-4}	0.862	205×10^{-4}	—	—	2.10	81.5×10^{-4}

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Arthur W. Etchells, Chairman, Hellwig Dyeing Corp., Delaware Ave. and Comly St., Philadelphia, Pa.
A. E. Raimo, Secretary, John Campbell & Co., S. E. Corner Broad and Spring Garden Sts., Philadelphia 23, Pa.
Curt R. Baeringer, Vice-Chairman; W. F. Fancourt, 3rd, Treasurer

Piedmont Section

Sidney M. Cone, Chairman, Proximity Manufacturing Co., Greensboro, N. C.
John B. Neely, Secretary, Burlington Mills, Yarn Dyeing Div., Burlington, N. C.
Leland G. Atkins, Vice-Chairman; Wyss L. Barker, Treasurer

South Central Section

Frank F. Myers, Chairman, Geigy Co., 700 Belvoir Ave., Chattanooga, Tenn
W. K. Newman, Secretary, Peerless Woolen Mills, Rossville, Ga.
W. P. Clements, Vice-Chairman; G. R. Bellamy, Treasurer

Midwest Section

Al. J. Feit, Chairman, E. I. duPont de Nemours & Co., Inc. 7 S. Dearborn Street, Chicago, Ill.
George B. Chabot, Jr., Secretary, Calco Chemical Division, American Cyanamid Co., 146 W. Kinzie Street, Chicago, Ill.
George E. Osha, Vice-Chairman; Joseph H. Jones, Treasurer

South-Eastern Section

O. G. Edwards, Chairman, Avondale Mills, Sylacauga, Ala.
W. B. Griffin, Secretary, Kali Manufacturing Co., 939 Highland Terrace, N. E. Atlanta, Ga.
J. E. Smenner, Vice-Chairman; Laurie E. Whittelsey, Treasurer

STUDENT CHAPTERS

Lowell Textile Institute
North Carolina State College
Philadelphia Textile Institute
New Bedford Textile School

Members should notify the Secretary immediately of all address changes

♦ ***Victory Convention, January 3, 4 and 5, 1946*** ♦

151st COUNCIL MEETING

Meeting Held in New York on October 5th—Several Proposals to Be Submitted to Letter Ballot—Appropriation for Revision of Colour Index—General Meeting Approved

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G. P. Callaway	R. T. Nazzaro
C. S. Chang	A. G. Noel
H. L. Cohen	A. C. Nuessle
K. DeCesare	O. Padula
M. Deker	L. Perno
W. J. Doody	E. S. Pierce
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H. R. Eckard	E. A. Heall
W. E. Edgar	L. M. Reynolds
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F. Fordemwalt	R. D. Robinson
D. J. Fox	M. H. Rorke
W. G. Fulton	C. E. Schafranek
V. U. Grose	W. Schulman
O. H. Grulke	I. R. Schwartz
F. H. Heiss	A. Sobocinski
F. W. Hellmann	R. H. Thornton
B. C. Holst	E. E. Tobin
W. P. ter Horst	H. W. Vahlteich
J. B. Irvine	P. Vaterrodt
L. H. Jackson	H. L. vonGoehde
G. D. Jefferson	E. A. Waring
R. G. Kavanagh	W. L. Williams
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	W. Windus

STUDENT

M. T. Ball	C. A. Norek

Respectfully submitted,
HAROLD C. CHAPIN, *Secretary*

SECRETARY'S FINANCIAL REPORT—SEPT. 28, 1945

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	*	**			
Miscellaneous items.....			Buttons	3.00	13.50
Reporters & Reprints....	5.75	21.75	Flammability testers		400.00
Year books	71.15	88.95	Publicity pamphlet	.25	
Crockmeters	73.00	194.00	Launderometer royalties .	140.00	25.00
Crock cloth	40.75	43.00	Testing service		
Multifiber cloth	39.00	1,026.00	Dividends	40.00	50.00
Moth cloth	25.00	16.75			
Water test apparatus....	65.00	254.00		664.90	
Dyed standards	149.00	145.00	Less bank charge.....	.06	
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Gas fading units.....	2.00	4.00		664.84	2,291.95

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VICTORY CONVENTION NEWS

COMMITTEES, VICTORY CONVENTION

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Norman A. Johnson
Printing, Personnel Service
Kenneth Barnard
Technical Program
Winn Chase
Publicity
S. M. Conn
General Reception

SUB-COMMITTEES

John H. Hennessey
Chairman, Registration Committee
Timothy Gibson
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John A. Cairns
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This set-up may be considered tentative, inasmuch as additional committees will be appointed if and as needed.

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The Chairman reported that Mr. Ryberg had resigned as Associate Director of Research to accept another position, but would remain a member of the Research Committee. He requested from each sub-committee, after each of its meetings, a complete report for his files, and a report marked for publication. He further requested notification of plans for meetings of sub-committees in connection with Research Committee meetings, three weeks in advance of such meetings. Availability of paper had now made possible the inclusion of dye lists in the 1945 Year Book. Analytical Methods would be bound separately and issued with the book. Plans for cooperation with the Society of Dyers and Colourists on a revised Colour Index were reported.

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variations in the same fabric and in humidity. Manner of brushing pile fabrics was an important factor, still under investigation. At Princeton Knitting Mills Mr. Young had found that shearing but .003 of an inch from one fabric made the difference between danger and safety.

Mr. Scull reported that the Committee on Atmospheric Fading of Dyed Acetate Rayon had found porosity of fabric such an important factor as to warrant dyeing of a standard strip with the blue dye previously adopted as a standard. Rolls of this, put up in glass jars, were to be provided by the committee for sale, by the Secretary of the Association, at two dollars each. Though the committee had designed a new testing oven, of which he showed photographs, it preferred thus far to formulate test methods solely in terms of the standard fabric, without reference to construction of the testing oven. Dr. Hager suggested, with approval of the meeting, that dyed standards for comparison with the faded sample be included with the rolls.

Respectfully submitted,
HAROLD C. CHAPIN, *Secretary*

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MEETING, SOUTHEASTERN SECTION

THE next meeting of the Southeastern Section will be held at the Atlanta Athletic Club, Atlanta, Ga., on Saturday evening, December 15th. The meeting hour and program will be announced at a later date.

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NOMINATIONS, SOUTHEASTERN SECTION

THE nominating committee of the Southeastern Section, composed of the following members: Earle Mauldin, chairman, Robert W. Philip, Curt Mueller, James A. Britton and George E. Missbach, have offered the following nominations for 1946:

A. Kempton Haynes, *Chairman*
Matthew T. Barnhill, *Vice-Chairman*
Dr. Howard M. Waddle, *Secretary*
Allyn J. Morse, *Treasurer*
William B. Griffin, *Councilor*
Robert O. Simons, *Sectional Committee*
Henry Louis Dozier
Sectional Committee
James C. Farrow, Jr.
Sectional Committee
Norman P. Arnold, *Sectional Committee*

— ♦ ♦ —

MEETING, PHILADELPHIA SECTION

A MEETING of the Philadelphia Section was held on Friday evening, October 19th, 1945, in the North Roof Garden at The Bellevue-Stratford Hotel.

Councilor James P. Conaway, advised the group as to the coming convention in New York City, January 3, 4, and 5.

Arthur W. Etchells appointed a nominating committee for new officers for 1946 as follows: Richard L. Jones, James Dixon and Edward C. Diehl.

Prof. Harvery A. Neville's subject, "Emulsions and Their Applications to Textiles" was received with great enthusiasm.

There were 170 present for dinner and 205 attending the meeting.

Respectfully submitted.
A. E. RAIMO, *Secretary*

Keep These Dates Open
January 3, 4 and 5, 1946
VICTORY CONVENTION
Auspices: New York Section

MEETING, RHODE ISLAND SECTION

THE next meeting of the Rhode Island Section will be held on November 23rd at the Providence Engineering Society Hall, 195 Angell Street, Providence, R. I. The speaker and subject are as follows: Prof. Edward R. Schwarz, Head, Textile Division, Massachusetts Institute of Technology: "Electronics for Textiles."

● CALENDAR OF COMING EVENTS ●

Meeting, South Central Section, Patten Hotel, Chattanooga, Tenn., November 10, 1945.

Meeting, Rhode Island Section, Providence Engineering Society Hall, 195 Angell Street, Providence, R. I., November 23, 1945.

Meeting, Philadelphia Section, November 30, 1945.

Meeting, Southeastern Section, Atlanta Athletic Club, Atlanta, Ga., December 15, 1945.

Victory Convention under auspices of New York Section, Hotel Pennsylvania, New York City, January 3rd, 4th and 5th, 1946.

Council Meeting, Hotel Pennsylvania, New York City, January 3, 1946.

Meetings of Sub-Committees of Research Committee, Hotel Pennsylvania, New York City, January 3, 1946.

President's Corporate Membership Dinner, Hotel Pennsylvania, New York City, January 3, 1946.

Research Committee Meeting, Hotel Pennsylvania, New York City, January 5, 1946.

Intersectional Contest, Hotel Pennsylvania, New York City, January 5, 1946.

Award of Olney Medal and Awards of Intersectional Contest Prizes, Hotel Pennsylvania, New York City, January 5, 1946.

Meeting, New York Section, Downtown Athletic Club, 19 West Street, New York City, February 1, 1946.

PERSONNEL SERVICE

Employers and members of the Association seeking employment can make appointments at the Victory Convention for interviews between noon on Thursday, January 3, and noon on Saturday, January 5.

Those seeking positions should file their qualifications well in advance of the meeting. Blanks can be obtained from the Secretary, P. O. Box 28, Lowell, Mass. Two photographs, approximately 2 by 2½ inches, will be required.

DATA ON WOOL-ACID-WATER RELATIONSHIPS

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WOOL-ACID "TITRATION" DATA

When a protein is dissolved, dispersed, or immersed in a solution containing a known amount of acid, and the solution is tested either for total acidity by titration with a base, or for hydrogen-ion concentration by potentiometric or colorimetric methods, less acid is found than was originally present. Further, if the protein-acid-water system is allowed sufficient time to reach equilibrium, the amount of an acid missing from the bath at a given end hydrogen-ion concentration is constant within experimental error. From data obtained by adding varying quantities of an acid to a number of baths containing a fixed amount of wool (largely composed of the protein, keratin), and determining the apparent loss of acid from the bath, "titration" or equilibrium curves may be plotted which illustrate the loss of acid as a function of pH—curves which should be instructive in the study of the basic dissociation of wool.*

In an effort to establish the stoichiometric nature of acid-protein combination, Loeb[1] ran a series of experiments with several proteins (egg albumin, gelatin, casein) and four strong acids: monobasic hydrochloric, dibasic sulfuric and oxalic, and tribasic phosphoric. He selected these acids because below pH 4 only sulfuric of the polybasic acids has a significant per cent of all its hydrogen equivalents dissociated, both the oxalic and phosphoric being practically monobasic in this range. At equilibrium, he found that approximately the same number of ccs. of N/10 hydrochloric and sulfuric acid had disappeared at the same pH, while approximately twice as many ccs. of N/10 oxalic, and three times as many ccs. of N/10 phosphoric acid had disappeared under the same conditions, proving his contention.

Comparison of these very interesting results with similar data on wool-acid-water relationships seemed very desirable as a preliminary step in establishing empirically the dissociation of wool as a base.**

* For a theoretical discussion of the acid and basic dissociation of wool as a function of pH, see K. LaFleur, Am. Dyestuff Reptr. 34, 21 (1945).

** At the time these experiments were planned and carried out, the author did not know that Speakman[2] had already reported on similar work. The publications of Harris and co-workers[3, 4] were at hand, and also serve in several ways to make this report seem superfluous. However, the experiments were undertaken when skepticism about the stoichiometric relationships of wool and water solutions of acids, bases and salts was too strong to be dissipated by the resuls of other investigators; in addition, they are merely a portion of a broader plan for the investigation of wool behavior, in which it is desirable to maintain continuity. In a field as young as this, having relatively few spokesmen, independently conceived experiments which lead to a duplication of data are perhaps of sufficient value not to require further apology.

EXPERIMENTAL PROCEDURE

Sets of swatches for preliminary experiments (Set I in the data which follow, in all four cases) were cut from a scoured 12 oz. fabric woven from a blend of 30 per cent Cape wool, and 70 per cent shorn Australian wool. The petroleum ether extraction residue from this fabric was 0.17 per cent, the ethyl alcohol extraction residue, 0.95 per cent; and total ash on ignition was 0.38 per cent.

Swatch weights were adjusted to 2.5 grams (oven dry basis) by balancing against a standard swatch cut from the same piece. The standard swatch was prepared by drying to constant weight at 110° C, steaming in open air until moist, and then allowing to reach equilibrium with moisture in the air from the wet side under the same conditions as the untreated swatches. The accuracy of this method was tested by oven-drying swatches weighed days apart, and the maximum error obtained was 0.9 per cent; the average deviation from the standard weight was ±0.3 per cent.

Cloth was chosen for the experiments rather than stock after some deliberation, as a matter of convenience in conditioning, weighing, and manipulating; because it was readily available and because a represenative sample of shorn wool in the grease was not at hand.

Sets of swatches for the verifying experiments (Set II in all four cases)† were cut from a weave room heading of a 13 oz. fabric, woven from a blend of 35 per cent noils, and 65 per cent shorn Australian wool. This cloth was immersed in successive petroleum ether baths at room temperature, soaked and manipulated until no further discoloration was apparent, dried at about 140° F, rinsed in warm water until clear, and placed under running water at faucet temperature for 3-4 hours.

† These verifying experiments were done in duplicate.

The petroleum ether extraction residue on this fabric was 0.14 per cent; the ethyl alcohol extract, 0.74 per cent. Total ash on ignition was 0.34 per cent.

To give an experimental bath of known volume from which an aliquot could be taken for titration, and still allow prewetting of the cloth, sample swatches were thoroughly wet, wrung individually between paper towelling in a wringer used for all further experiments, and weighed. The average increase in weight over the oven-dry weight was used to adjust the indicating line of a 250 ml. volumetric flask, which would insure a 250 ml. (1/100) bath after entering the damp cloth. The correction applied was 2.7 ccs.

All four sets of acid baths were adjusted to approximate initial pHs of 4.0, 3.5, 3.0, 2.8, 2.6, 2.4, 2.2, 2.0, 1.8, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1 1.0, to make comparisons easier. Wherever possible the quantities of acid added to obtain these pHs were read from dissociation curves plotted from data collected and published by Wilson[5]. Other quantities were read from extensions of these curves plotted from data obtained in this laboratory, using untreated water and LaMotte pH indicator sets.

Pre-wet swatches, wrung as described above, were entered in Erlenmeyer flasks containing acid baths at room temperature, and the flasks were swirled and stoppered. The swatches were left in the baths for a minimum of 15 hours‡, at room temperature (24°±4° C), with occasional swirling. In almost all cases immersion times were longer; one set of oxalic acid experiments was titrated a full day later than the duplicate set, and results agree well.

At the end of the soaking period, swatches were pulled up into the neck of the flask, allowed to drip, and were discarded. 200 ml. aliquots of the low acidity baths, and duplicate 100 ml. aliquots of the more concentrated baths were titrated against standard NaOH. The pH of the baths was determined with LaMotte indicator sets.

All normality factors were based on repeated periodic standardizing of a stock

‡ Previous experiments have shown this to be ample time to attain equilibrium in a wool-mineral acid-water system at room temperature. The oxalic acid equilibrium was tested as stated above.

TABLE 1. Wool-Hydrochloric Acid-Water Relationships

SET I

No.	Initial pH*	Ccs. N/10 HCl Used per 100ccs.	Ccs. N/10 HCl Found in Bath at Equilibrium	Ccs. N/10 HCl which Disappeared from Bath	Final pH*	Final pH (LaMotte)
1.	3.5	0.5	0.03	0.47	...	6.4
2.	3.22	0.7	0.05	0.65	...	6.35
3.	3.0	1.0	0.08	0.92	...	5.6
4.	2.81	1.5	0.13	1.37	...	4.45
5.	2.61	2.45	...	...	...	...
6.	2.4	3.9	1.43	2.47	2.83	2.9
7.	2.19	6.3	2.49	3.81	2.60	2.6
8.	2.0	10	5.06	4.94	2.28	2.25
9.	1.79	15.8	9.24	6.56	2.03	2.0
10.	1.55	29	21.6	7.4	1.67	1.7
11.	1.5	32.5	24.9	7.6	1.61	1.65
12.	1.4	40.5	32.4	8.1	1.51	1.55
13.	1.29	53	44.6	8.4	1.36	1.4
14.	1.21	65	...	...	...	...
15.	1.1	83	74.4	8.6	1.14	...
16.	1.02	100	90.7	9.3	1.07	...

* Read from the hydrochloric acid dissociation curve.

TABLE 2. Wool-Hydrochloric Acid-Water Relationships

SET II

No.	Initial pH*	Ccs.N/10 HCl Used per 100ccs.	Ccs. N/10 HCl Found in Bath at Equilibrium	Ccs. N/10 HCl which Disappeared from Bath	Final pH*	Final pH (LaMotte)
1.	4.06	0.36	0.11	0.25	...	6.65
			0.08	0.28	...	6.65
2.	3.5	0.50	0.15	0.35	...	6.5
			0.10	0.40	...	6.5
3.	3.0	1.0	0.16	0.84	...	5.55
			0.13	0.87	...	5.55
4.	2.81	1.5	0.21	1.29	...	4.6
			0.23	1.27	...	4.5
5.	2.6	2.46	0.5	1.96	3.50	3.45
			0.47	1.99	3.58	3.45
6.	2.4	3.9	1.17	2.73	2.92	2.9
			1.17	2.73	2.92	2.9
7.	2.19	6.3	2.6	3.7	2.58	2.6
			2.65	3.65	2.57	2.6
8.	2.0	10	5.09	4.91	2.28	2.3
			5.13	4.87	2.28	2.3
9.	1.79	15.8	9.75	6.05	2.0	1.95
			9.8	6.0	2.0	1.95
10.	1.55	29	21.2	7.8	1.67	1.65
			21.6	7.4	1.67	1.65
11.	1.5	32.5	24.8	7.7	1.61	1.6
			25	7.5	1.61	1.6
12.	1.4	40.5	32.1	8.4	1.51	1.5
			32.3	8.2	1.51	1.5
13.	1.29	53	44	9.0	1.37	1.4
			44.3	8.7	1.36	1.4
14.	1.21	65	55.7	9.3	1.27	...
			56	9.0	1.27	...
15.	1.1	83	72.9	10.1	1.16	...
			73.4	9.6	1.15	...
16.	1.03	96.1	86	10.1	1.08	...
			86.5	9.6	1.08	...

* Read from the hydrochloric acid dissociation curve.

TABLE 3. Wool-Sulfuric Acid-Water Relationships

SET I

No.	Initial pH*	Ccs. N/10 H_2SO_4 Used per 100ccs.	CCc. N/10 H_2SO_4 Found in Bath at Equilibrium	Ccs. N/10 H_2SO_4 which Disappeared from Bath	Final pH*	Final pH (LaMotte)	Ccs. M/10 H_2SO_4
1.	4.0	0.37	0.04	0.33	...	6.45	0.17
2.	3.5	0.60	0.06	0.54	...	6.3	0.27
3.	3.0	1.25	0.10	1.15	...	5.1	0.58
4.	2.8	1.65	0.13	1.52	...	4.85	0.76
5.	2.6	2.5	0.23	2.27	...	4.0	1.14
6.	2.4	4.25	0.58	3.67	3.52	3.35	1.84
7.	2.2	7.0	1.85	5.15	2.73	2.7	2.58
8.	2.0	12	5.3	6.7	2.32	2.3	3.35
9.	1.8	20	12.5	7.5	1.98	2.0	3.75
10.	1.6	34.5	26.1	8.4	1.7	1.75	4.2
11.	1.5	45	36.7	8.3	1.58	1.55	4.15
12.	1.41	57	48.3	8.7	1.47	1.45	4.35
13.	1.3	76	67	9.0	1.34	1.4	4.5
14.	1.22	95.9	87.6	8.3	1.25	1.3	4.15
15.	1.12	12.5**	11.4**	11	1.15	1.2	5.5
16.	1.02	16	14.6	14	1.05	...	7.0

* Read from the sulfuric acid dissociation curve.
** N H_2SO_4.

TABLE 4. Wool-Sulfuric Acid-Water Relationships

SET II

No.	Initial pH*	Ccs. N/10 H_2SO_4 Used per 100ccs.	Ccs. N/10 H_2SO_4 Found in Bath at Equilibrium	Ccs. N/10 H_2SO_4 which Disappeared from Bath	Final pH*	Final pH* (LaMotte)	Ccs. M/10 H_2SO_4
1.	4.0	0.37	0.03	0.34	6.7	6.8	0.17
			0.02	0.35	6.8	6.65	0.18
2.	3.5	0.60	0.03	0.57	6.7	6.6	0.29
			0.02	0.58	6.8	6.6	0.29
3.	3.0	1.25	0.09	1.16	6.45	5.3	0.58
			0.10	1.15	6.4	5.8	0.58
4.	2.8	1.65	0.09	1.56	6.45	4.5	0.78
			0.12	1.53	6.3	4.45	0.77
5.	2.6	2.5	0.22	2.28	5.9	4.1	1.14
			0.24	2.26	5.6	4.2	1.13
6.	2.4	4.25	0.63	3.62	3.45	3.4	1.81
			0.63	3.62	3.45	3.35	1.81
7.	2.2	7.0	1.72	5.28	2.78	2.8	2.64
			1.66	5.34	2.8	2.8	2.67
8.	2.0	12	5.1	6.9	2.34	2.3	3.45
			5.05	6.95	2.34	2.35	3.48
9.	1.8	20	12.2	7.8	1.99	2.05	3.9
			12.4	7.6	1.99	2.05	3.8
10.	1.6	34.5	25.6	8.9	1.71	1.75	4.45
			26.2	8.3	1.69	1.75	4.15
11.	1.5	45	35.7	9.3	1.59	1.7	4.65
			36.2	8.8	1.58	1.65	4.4
12.	1.41	57	47.1	9.9	1.48	1.55	4.95
			48.3	8.7	1.47	1.55	4.35
13.	1.3	76	66.6	9.4	1.34	1.45	4.7
			67.2	8.8	1.34	1.45	4.4
14.	1.2	100	88.7	11.3	1.24	1.35	5.65
			91.2	8.8	1.23	1.35	4.4
15.	1.1	13**	12**	10	1.13	1.3	5.0
			12.1	9.0	1.13	1.3	4.5
16.	1.0	16.7	15.7	10	1.02	1.2	5.0
			15.8	9.0	1.02	1.2	4.5

* Read from the sulfuric acid dissociation curve.
** N H_2SO_4.

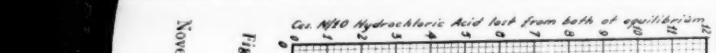


TABLE 5. Wool-Oxalic Acid-Water Relationships

SET I

No.	Initial pH*	Ccs. N/10 Oxalic Used per 100ccs.	Ccs. N/10 Oxalic Found in Bath at Equilbirium	Ccs. N/10 Oxalic which Disapeared from Bath	Final pH*	Final pH (LaMotte)	Ccs. M/10 Oxalic
1.	4.0	0.45	0.05	0.40	...	...	0.2
2.	3.5	0.97	0.10	0.87	6.4	...	0.44
3.	3.0	2.4	0.24	2.16	4.5	...	1.08
4.	2.8	3.6	0.90	2.7	3.55	3.5	1.35
5.	2.6	5.45	1.38	4.07	3.3	...	2.04
6.	2.4	8.4	3.28	5.12	2.84	...	2.56
7.	2.2	14	7.24	6.76	2.47	...	3.38
8.	2.0	24	15.4	8.6	2.16	...	4.3
9.	1.8	40	30.2	9.8	1.9	...	4.9
10.	1.6	70	58.8	11.2	1.67	...	5.6
11.	1.5	94	80.4	13.6	1.55	...	6.8
12.	1.4	13.2**	11.7 *	15	1.43	...	7.5
13.	1.3	18.8	17	18	1.33	...	9
14.	1.2	28	26	20	1.22	...	10
15.	1.1	40	36.8	32	1.13	...	16
16.	0.9	74	70.4	36	0.92	...	18

* Read from the oxalic acid dissociation curve.
** N COOH
|
COOH

Table 6. Wool-Oxalic Acid-Water Relationships

SET II

No.	Initial pH*	Ccs. N/10 Oxalic Used per 100ccs.	Ccs. N/10 Oxalic Found in Bath at Equilibrium	Ccs. N/10 Oxalic which Disappeared from Bath	Final pH*	Final pH (LaMotte)	Ccs. M/10 Oxalic
1.	4.0	0.45	0.14	0.31	6.2	6.4	0.16
			0.08	0.37	...	6.65	0.19
2.	3.5	0.97	0.10	0.87	6.4	5.5	0.44
			0.13	0.84	6.25	6.25	0.42
3.	3.0	2.4	0.33	2.07	4.6	4.0	1.04
			0.33	2.07	4.6	4.1	1.04
4.	2.8	3.6	0.74	2.86	3.67	3.6	1.43
			0.71	2.89	3.7	3.6	1.45
5.	2.6	5.5	1.68	3.82	3.18	3.1	1.91
			1.6	3.90	3.21	3.1	1.95
6.	2.4	8.4	3.37	5.03	2.82	2.8	2.52
			3.25	5.15	2.84	2.7	2.58
7.	2.2	14	7.2	6.8	2.47	2.45	3.4
			7.1	6.9	2.48	2.5	3.45
8.	2.0	23.3	14.6	8.7	2.18	2.15	4.35
			14.7	8.6	2.18	2.15	4.3
9.	1.8	40	29	11	1.92	1.9	5.5
			28.9	11.1	1.92	1.9	5.56
10.	1.6	70	56.6	13.4	1.67	1.65	6.7
			56.8	13.2	1.68	1.65	6.6
11.	1.5	94	80.2	13.8	1.55	1.55	6.9
			80.1	13.9	1.55	1.55	6.95
12.	1.4	13.2**	11.7**	15	1.43	1.45	7.5
			11.7	15	1.43	1.45	7.5
13.	1.3	18.8	17.1	17	1.33	1.3	8.5
			17.1	17	1.33	1.35	8.5
14.	1.2	28	26.2	18	1.22	1.25	9.0
			26.3	17	1.22	1.25	8.5
15.	1.1	40	38.1	19	1.12	1.1	9.5
			38.1	19	1.12	1.05	9.5
16.	0.9	74	71.4	26	0.91	0.95	13
			71.7	23	0.91	0.9	11.5

* Read from the oxalic acid dissociation curve.
** N COOH
|
COOH

solution of N/10 sulfuric acid against sodium carbonate with phenophthalein as an indicator.

Methyl orange was used in the phosphoric acid titrations.

Data (tables 1-8) and curves (figures 1-6) follow. The extent to which the polybasic acids dissociate off more than one hydrogen-ion is roughly illustrated by the curves of figure 5. Only sulfuric acts largely as a dibasic acid toward wool. The data agree approximately with those obtained by Loeb.

POTENTIAL SOURCES OF ERROR

La Motte indicator readings were made with pH sets in which there is a considerable overlapping of individual indicators, making it possible to check many readings. The readings taken in the middle of a given indicator range were considered most reliable. Though the pH thus determined is given to .05 pH unit, the probable error is no less than ±.05 pH unit.

In titrating both the very high and very low acidity baths, the possibility of error is much greater than in titrations over the middle range. It would be difficult to assign even a semi-quantitative probable error to such titrations. Calling attention to the difficulties is all that can be done here.

Several experiments have indicated that some hydrolysis of wool protein occurs even in low temperature-low acidity baths, during short immersion periods. In baths of high acidity, this decomposition probably becomes a significant source of error; to this factor may be attributed some of the anomalous and variable results obtained around pH 1. Again it is impossible to assign a probable error, because too little is known of all the ramifications.

Within the limitations indicated above, and others not mentioned (and doubtless

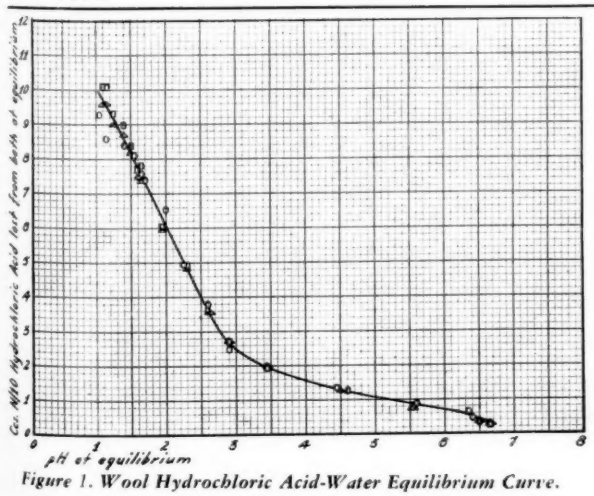


Figure 1. Wool Hydrochloric Acid-Water Equilibrium Curve.

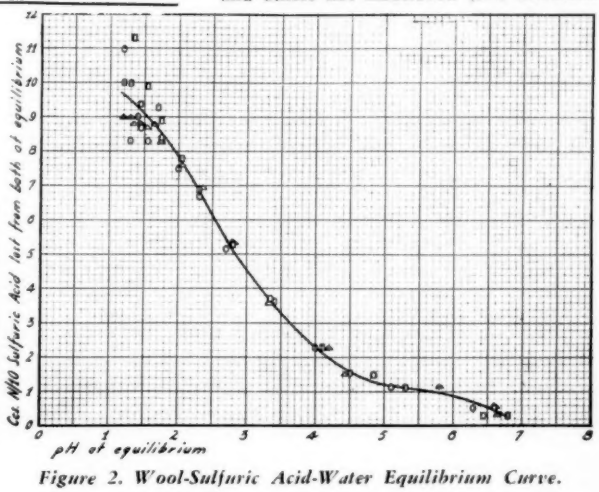


Figure 2. Wool-Sulfuric Acid-Water Equilibrium Curve.

Table 7. Wool-Phosphoric Acid-Water Relationships
SET I

No.	Initial pH*	Ccs. N/10 H_3PO_4 Used per 100ccs.	Ccs. N/10 H_3PO_4 Found in Bath at Equilibrium	Ccs. N/10 H_3PO_4 which Disappeared from Bath	Final pH*	Final pH (LaMotte)	Ccs. M/10 H_3PO_4
1.	4.0	...	...	...	...	...	...
2.	3.81	1.09	0.2	0.89	6.35	6.5	0.30
3.	3.05	3.18	0.6	3.12	5.55	5.1	1.04
4.	2.8	...	...	...	...	...	...
5.	2.63	9.09	3.02	6.07	3.07	3.0	2.02
6	2.44	15.5	7.52	7.98	2.69	2.65	2.66
7.	2.23	29.1	18.5	10.6	2.37	2.35	3.53
8.	2.04	54.5	41.8	12.7	2.11	2.1	4.23
9.	1.87	10.3**	8.75**	16.5	1.90	1.9	5.5
10.	1.62	23.4	21.4	20	1.65	1.6	6.67
11.	1.52	32.8	30.8	20	1.54	1.55	6.67
12.	1.42	45.0	42.6	24	1.43	1.45	8.0
13.	1.32	63.7	61.5	22	1.33	1.4	7.33
14.	1.22	86.2	84	22	1.23	1.3	7.33

* Read from the phosphoric acid dissociation curve.
** N H_3PO_4.

Table 8. Wool-Phosphoric Acid-Water Relationships
SET II

No.	Initial pH*	Ccs. N/10 H_3PO_4 Used per 100ccs.	Ccs. N/10 H_3PO_4 Found in Bath at Equilibrium	Ccs. N/10 H_3PO_4 Which Disappeared from Bath	Final pH*	Final pH (LaMotte)	M/10 H_3PO_4
1.	3.85	1.07	0.15	0.92	6.4	6.35	0.31
			0.15	0.92	6.4	6.55	0.31
2.	3.44	1.63	0.29	1.34	6.2	6.05	0.45
			0.29	1.34	6.2	6.1	0.45
3.	3.0	3.56	0.6	2.96	5.55	4.2	0.99
			0.6	2.96	5.55	4.15	0.99
4.	2.8	5.91	1.67	4.24	3.42	3.3	1.41
			1.59	4.32	3.46	3.3	1.44
5.	2.6	10.2	4.41	5.79	2.9	2.9	1.93
			4.41	5.79	2.9	2.85	1.93
6.	2.4	17.3	9.6	7.7	2.61	2.7	2.58
			9.68	7.62	2.6	2.6	2.54
7.	2.2	32.6	22.7	9.9	2.3	2.3	3.3
			22.6	10	2.31	2.3	3.33
8.	2.0	61.2	49.6	11.6	2.06	2.1	3.87
			49.8	11.4	2.06	2.1	3.8
9.	1.84	11.3**	9.41**	18.9	1.88	1.9	6.3
			9.45	18.5	1.88	1.9	6.17
10.	1.6	25.6	23.3	23	1.63	1.65	7.67
			23.6	20	1.63	1.65	6.67
11.	1.49	35.8	33.6	22	1.51	1.55	7.33
			33.6	22	1.51	1.55	7.33
12.	1.39	49.2	47.2	20	1.41	1.45	6.67
			47.1	21	1.41	1.45	7.0
13.	1.28	69.6	67.5	21	1.3	1.35	7.0
			67.4	22	1.3	1.35	7.33
14.	1.19	94.2	91.7	25	1.21	1.25	8.33
			92.0	22	1.2	1.25	7.33

* Read from the phosphoric acid dissociation curve.
** N H_3PO_4.

some not thought of), the data presented are as reliable as care could make them.

CORRECTING THE 'TITRATION' CURVES

In a previous paper[1] from this laboratory, the theroetical basis of wool dissociation as an acid and as a base was discussed, and curves were drawn representing the dissociation. Even if this interpetation were a strictly accurate description of the behavior of pure wool keratin, some deviation would be expected empirically. For example, it is mere wishful thinking to believe that the wool fiber, if reactive at all, is going to postpone activity until the researcher is ready to examine it. Every experiment starts with wool in which reactive groups are in some way modified, and probably the effects cannot be safely disregarded. Since a line must be drawn somewhere, the simple case of either a smaller total of carboxyl groups or amino groups (or both) can be assumed to be the net result of such complications; if the best figure obtainable is assigned to this revised amount, new curves representing the acid and basic dissociation of wool can be plotted. The ordinate difference between these curves and those plotted as if wool protein were pure will give a correction which can be applied to experimental data.

The further complications immediately arise that, while this approach is one which is justified in theory, the proper correction probably cannot be found; and if found, cannot be subtracted from truly representative wool dissociation curves, because they have yet to be determined.

A tentative correction can be made if these difficulties are solved conditionally:

(1). If the isoelectric point of wool is

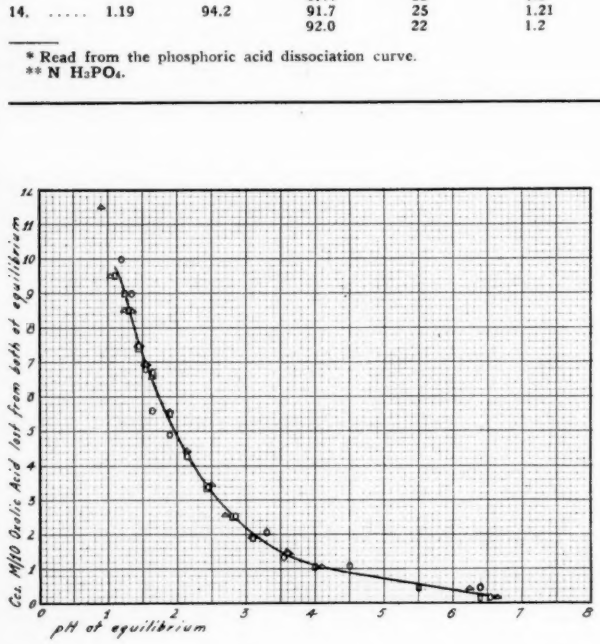


Figure 3. Wool-Oxalic Acid-Water Equilibrium Curve.

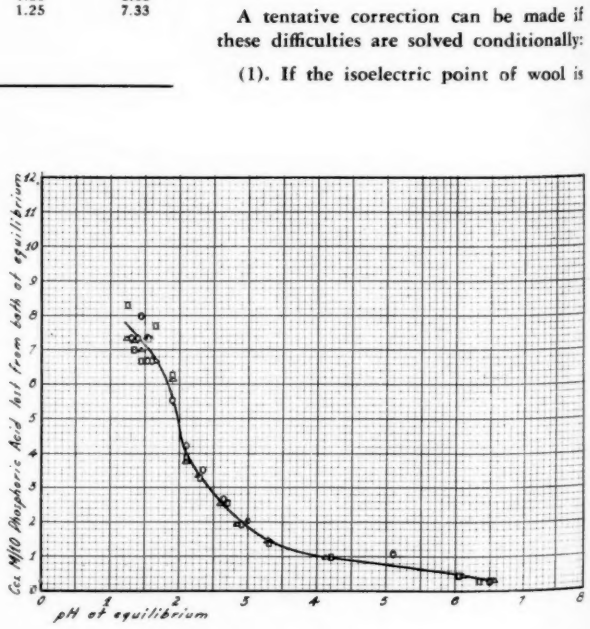


Figure 4. Wool-Phosphoric Acid-Water Equilibrium Curve.

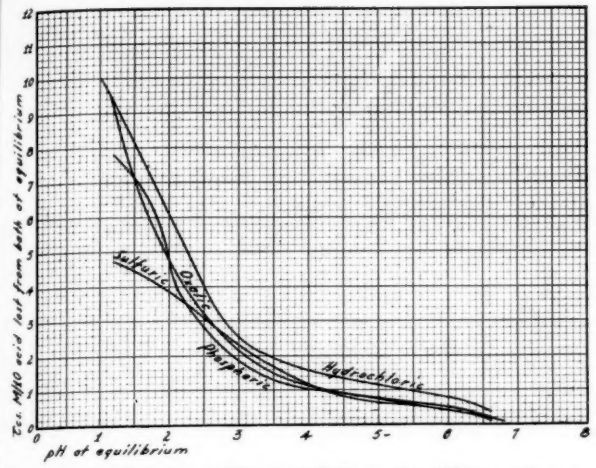


Figure 5. Comparison of Wool-Acid-Water Equilibrium Curves: Ccs. M/10 Acid Lost from Bath.

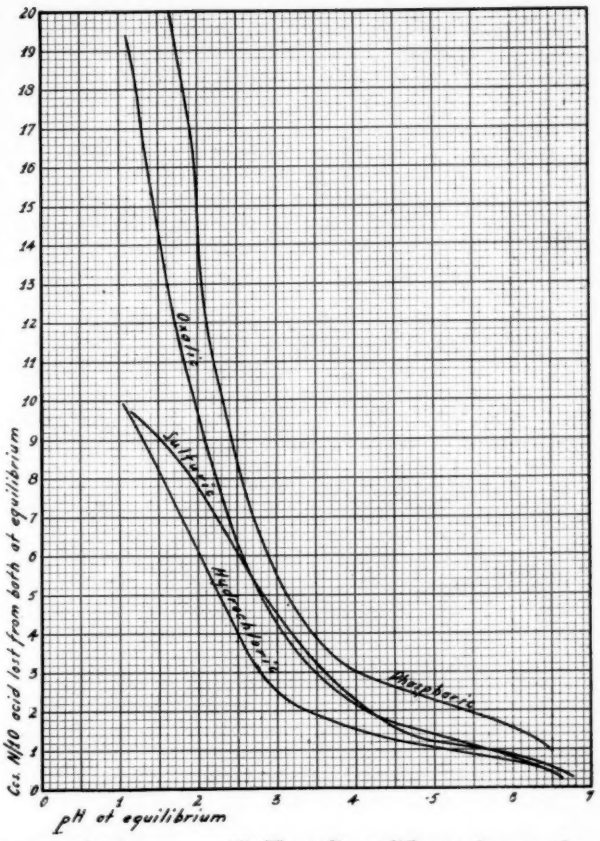


Figure 6. Comparison of Wool-Acid-Water Equilibrium Curves: Ccs. N/10 Acid Lost from Bath.

assumed to be at pH 5.0, and the acid dissociation curve is adjusted to allow this without changing the basic dissociation (which could be justified on such grounds as the possibility of the existence of less amide nitrogen then has been found experimentally, or the equivalent), a diagram representing the possible dissociation of wool as an acid and a base can be drawn which coincides better with empirical data than any of the three diagrams hitherto presented[6] (figure 7). This is of course quite arbitrary, and is presented only to aid in solving tentatively the problem being considered.

(2). Much of the inorganic ash of wool fibers consists of oxides of metallic cations assumed to have been bound in salt linkage to the 'free' acid (carboxyl) groups in wool. While organic or other volatile cations and anions can also be bound, and would not be present in the ash, it is usually tacitly assumed that they are not present in significant quantity in untreated wool. Two methods for determining the equivalence of the inorganic cations in wool are found in the literature[7,8]. The simpler consists of ashing the sample and titrating the ash. Using this method, 1 gram of wool used for the confirming (second) sets of experiments left a residue which was neutralized by 0.52 ccs. of N/10 acid.

(3). The ordinate difference between the basic dissociation (difference curve) of figure 7, and that of a revised basic dissociation (difference curve), obtained by plotting a new acid dissociation curve for wool having a total combining capavity less by .052 milli-equivalents than the theoretical combining capacity, can now be calculated as a function of pH

(Concluded on Page 452)

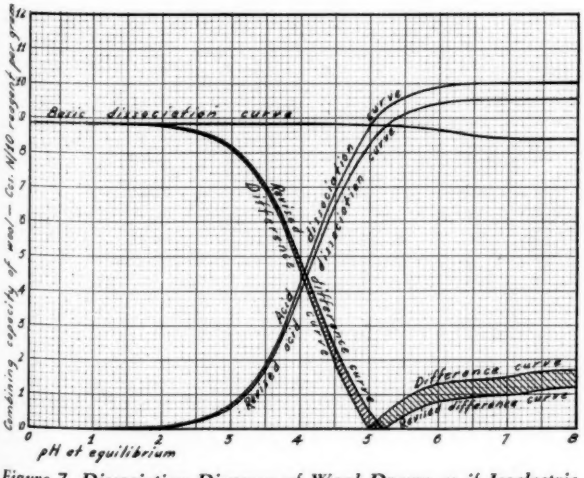

Combining capacity of wool — Ccs. N/10 reagent per gram
pH at equilibrium
Basic dissociation curve
Revised basic dissociation curve
Difference curve
Revised difference curve
Acid dissociation curve
Revised acid dissociation curve

Figure 7. Dissociation Diagram of Wool Drawn as if Isoelectric Point were at pH 5.0; and Corrected Dissociation Curves if Total Cation Combining Capacity is Reduced by .052 Milli-Equivalents per Gram of Wool.

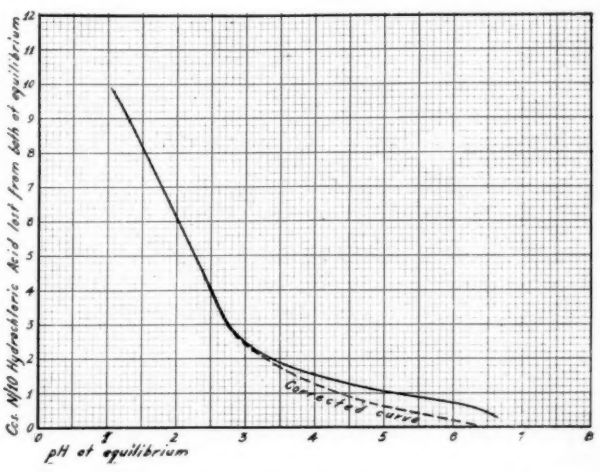


Figure 8. Wool-Hydrochloric Acid-Water Equilibrium Curve Corrected for Non-Volatile Cationic Ash.

The Absorption of Acid Dyes—

(Continued from Page 438)

pH values. Between pH 2.0 and 1.1 the solution becomes yellow-green to yellow. In colorimetric measurements, the dyebaths were suitably diluted and then made alkaline by adding 1 c.c. 0.880 ammonia per 100 c.c. of the final solution before measurement. The results obtained are given in Table V.

TABLE V

Absorption Isotherms of Disulphine Blue V 250* on Wool at Different pH Values
Acid—Sulfuric acid; Temperature 95°C.; Time 6 hr.; and Liquor-goods ratio 100:1

Initial Concentration in Dyebath (g. standard dye per l.)	Dyebath pH 6.1		Dyebath pH 1.2	
	Fibre (milli-equivalent per g.)	Dyebath (g-equivalents per l.)	Fibre (milli-equivalent per g.)	Dyebath (g-equivalents per l.)
0.1	0.001	1.2×10^{-4}	—	—
0.5	0.006	6.1×10^{-4}	0.028	3.8×10^{-4}
1.0	0.012	12.0×10^{-4}	0.054	7.8×10^{-4}
2.0	0.027	23.7×10^{-4}	0.125	13.8×10^{-4}
3.0	—	—	0.204	19.1×10^{-4}
4.0	0.053	47.4×10^{-4}	—	—
5.0	—	—	0.349	30.9×10^{-4}
5.0 (repeat)	—	—	0.359	29.9×10^{-4}
7.5	—	—	0.533	45.4×10^{-4}
10.0	0.092	122.0×10^{-4}	0.658	65.8×10^{-4}

* The dye has been assumed to act as a monobasic acid in this case. See discussion later.

THE SHAPE OF THE ISOTHERMS

In considering the shape of the absorption isotherms, the subject may be approached on the assumption that dyeing takes place by attachment of dye molecules to active centers in the wool. The mode of attachment may be by physical adsorption or chemical combination, but it must certainly be reversible in order to account for the phenomena of levelling. The rate of take-up of dye may be represented by—

$$K_1 C_B \ (A - C_F)$$

(C_B and C_F = the concentrations of dye in the dyebath and on the fiber, respectively; and A = the concentration of dye which would be attained if all the available sites were occupied by dye). $A - C_F$ is thus a measure of the number of sites still available to dye at any moment. At the same time dye is leaving the fiber for the aqueous phase and the rate of loss may be represented by $K_2 C_F$ (K_2 = a constant). At equilibrium the two rates are equal and thus—

$$K_1 C_B \ (A - C_F) = K_2 C_F$$

$$A \frac{C_B}{C_F} = \frac{K_2}{K_1} + C_B$$

$$\text{or } \frac{C_B}{C_F} = \alpha + \beta C_B \qquad (1)$$

(α and β = constants). Equation (1) represents a special case of the Langmuir adsorption isotherm.

Obviously, if the values of C_B/C_F are plotted against those of C_B, a straight line should result. In the above treatment the effect of other anions in the system, in competing with dye for the available sites, has been ignored. Assuming the presence of one other anion, e.g., sulfate, similar treatment leads to the equation—

$$\frac{C_B}{C_F} = \alpha + \beta C_B + \gamma C_{BS} \qquad (2)$$

(α, β and γ = constants; and C_{BS} = the concentration of sulfate anions in the dyebath). Equation (2) reduces to the simpler form (1) if the concentration of inorganic anions in the dyebath is maintained constant. In the present series of experiments this was not the case, for the dye itself was not pure, but contained some inorganic salt as diluent. It was anticipated, however, that the effect of the sulfate anions from the acid and the diluent in the dye would be small in view of their relatively low affinity for wool as compared with the affinity of the dye anions.

Accordingly, the results obtained were plotted using C_B/C_F and C_B as co-ordinates. Some of the results are illustrated in Figs. 4, 5, 6 and 7.

The results in all cases is along straight lines at the higher concentrations. The isotherms which are not shown also yield straight lines. It should be noted that the existence of a straight-line relationship at high dyebath concentrations is not very significant, for when the fiber is saturated, i.e. when C_F is constant, any increase in the dyebath concentrations is naturally followed by a proportionate increase in the ratio C_B/C_F. Many of the straight lines, however, extend to the region where the fiber is still not fully saturated with dye, and in this region provide support for the suggested

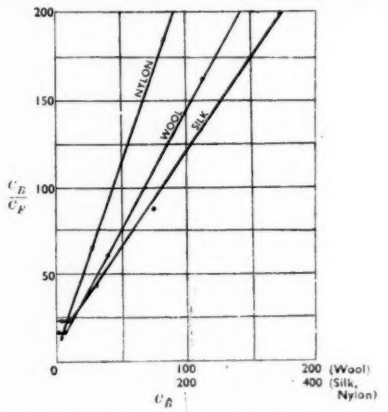


Fig. 4—Absorption of Solway Blue BS by Various Fibers.

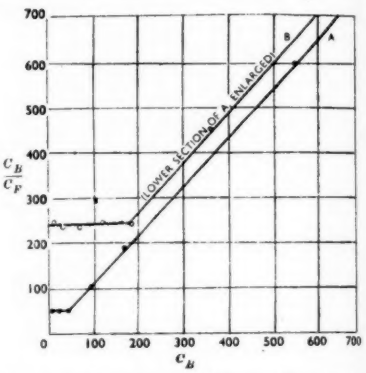


Fig. 5—Absorption of Solway Blue BS by Wool at pH 1.35.

In the top curve (B), the values of both sets of co-ordinates have been increased four-fold in order to show up the short horizontal portion of the curve (A).

Fig. 6—Absorption of Carbolan Blue BS by Wool.

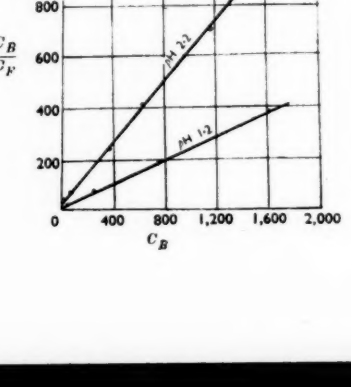
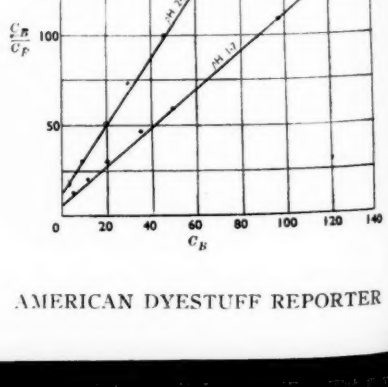


Fig. 7—Absorption of Carbolan Blue BS by Nylon.



relationship in the case of all the four different fibers.

In some cases, however, it was noted that at low concentrations the experimental points deviate from a straight line. The deviation takes the form of a second straight line representing a constant value of the ratio C_B/C_F. Examples where this has been observed are in the cases of the dyeing of wool with Solway Blue B at pH 1.35 and 1.6, and with Carbolan Blue B at pH 2.2, and of silk with Solway Blue B at pH 1.6. The constancy of this partition ratio at low concentrations seems to indicate that the dyebath is behaving as if a partition between two solvents is involved.

It is true that at low concentrations the Langmuir equation (1) tends towards a constant partition ratio, but this is only an approximation and all the points should lie upon the one straight line when C_B/C_F is plotted against C_B. Therefore, this deviation represents a real departure from equation (1).

By measurement on the graphs, the point at which the straight line representing the hyperbolic part of the curve intersects the straight line representing the constant partition may be determined, and with Solway Blue B it appears to occur with wool and silk at a point corresponding to two-thirds saturation of the fiber in both cases. After this point, with increasing dye in the dyebath, the absorption deviates towards the saturation value of the fiber. Two-thirds saturation of the fiber corresponds in the case of wool to a shade of 25 per cent standard Solway Blue BS on the weight of wool. As this is far above the strength of shade used in practical dyeing, it may be assumed that in the region of practical concentrations the partition ratio of dye between fiber and bath is independent of the dye concentration. In the case of silk, departure from linearity occurs at pH 1.6 with about 8 per cent of standard dye on the weight of fiber; this amount is also greater than is used in practice.

The experiments which have already been described were neither designed to measure very accurately the distribution of dye between fiber and bath at low concentrations, nor were a sufficient number of points determined in this region to provide adequate information on the anomalous behavior. Accordingly, further experiments were carried out to determine whether the constancy of partition could be more decisively established. The opportunity was also taken to investigate the effects of competing inorganic anions on the dyeing system, for it was thought that the observed behavior might be due to the additional term which is present in equation (2).

The approach was made from two directions. In the first place an investigation was made of the amount of dye removed from wool by a solution of sodium sulfate. This really involves approaching the equilibrium from the opposite side to dyeing, and has certain technical advantages, as will be evident from the description of the experiment. Four samples of wool were prepared, dyed with different quantities of Solway Blue BS by the normal dyeing method. The quantity of dye on the fiber was estimated from the exhaustion of the dyebath. From one of these dyeings a portion of wool weighing about 0.5 g. was taken and packed tightly into a test-tube. The wool was then covered with about 10 c.c. of 0.1M-sodium sulfate, the tube tightly corked and placed in a thermostat at 62° C. The material was stirred vigorously at frequent intervals. After 2 hr. the wool was removed and a second sample of wool from the same original dyeing was placed in the residual liquor. Since this liquor had already been brought to equilibrium with wool of almost the same dye concentration, the amount of dye which had to bleed out of the second sample was negligible, so that the dye concentration on the fiber was assumed to be unchanged. Further, equilibrium was rapidly established, and the formation of a concentration gradient inside the fiber was avoided. The use of this technique was suggested by Dr. G. A. Gilbert. After 1 hr. at 62° C., the second sample of wool was removed and the quantity of dye in the solution estimated. The results obtained are given in Table VI.

TABLE VI
Desorption of Wool Dyed with Solway Blue BS by 0.1M-Sodium Sulfate at 62° C.

C_F (millequivalent of dye per g. of fiber)	C_B (g.-equivalents of pure dye per l. of liquor)	C_B/C_F
3.6×10^{-4}	6.8×10^{-7}	1.9×10^{-3}
6.2×10^{-4}	12.6×10^{-7}	2.0×10^{-3}
11.2×10^{-4}	22.0×10^{-7}	2.0×10^{-3}
13.8×10^{-4}	28.2×10^{-7}	2.0×10^{-3}

These results provide confirmation of the existence of a constant value of C_B/C_F at low concentrations, and indicate that the discrepancies observed in the absorption isotherms are real and represent a deviation from equation (1).

In addition, dyeing experiments were carried out with Disulphine Blue V 250 at 95° C., using different quantities of Glauber's salt in the dyebath. The pH of the solutions was 2.2 and the other conditions were as described in the earlier experiments with this dye, except that numerous measurements were made at low concentrations and the absorption was estimated by examining the exhausted dyebath rather than the dyeings themselves, so that accuracy was relatively greater at low concentrations than at high concentrations. The results are given in Table VII, in which the value of the partition coefficient C_B/C_F is also given, and illustrated in Figs. 8 and 9.

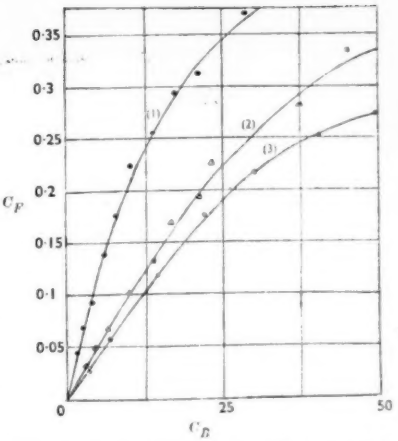


Fig. 8—Absorption of Disulphine Blue V250 by Wool at Different Glauber's Salt Concentrations.
(1) Dyebath containing 0.0031 moles Na_2SO_4 per l.
(2) Dyebath containing 0.0155 moles Na_2SO_4 per l.
(3) Dyebath containing 0.031 moles Na_2SO_4 per l.
C_F = Dye on Fiber, in milliequivalent per g.
C_B = Residual Dye in Bath, in g.-equivalents per l.

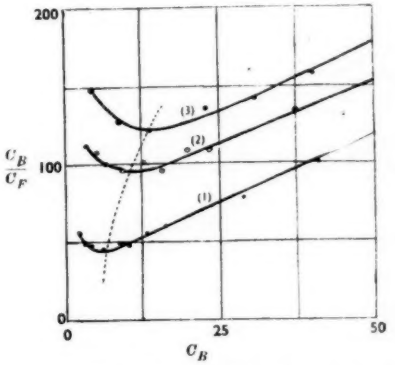


Fig. 9—Absorption of Disulphine Blue V250 by Wool at Different Glauber's Salt Concentrations.
(1) Dyebath containing 0.0031 moles Na_2SO_4 per l.
(2) Dyebath containing 0.0155 moles Na_2SO_4 per l.
(3) Dyebath containing 0.031 moles Na_2SO_4 per l.

From Table VII and Fig. 9 it is evident that the same anomalous behavior is observed. There is some indication of an increase in the value of C_B/C_F at low concentrations; this is scarcely within the limits of experimental error and is consistently present in all four curves. As the quantity of sulfate ion in the dyebath is increased, the concentration of dye in the fiber is reduced, owing to competition between sulfate and dye anions for the available sites, and the region over which

TABLE VII

Absorption Isotherms of Disulphine Blue V-250* on Wool at Various Ionic Concentrations
Acid—Sulfuric acid; Temperature 95°C.; Time 6 hr.; Liquor-goods Ratio 100:1; and pH 2.2

Initial Concentration in Dyebath (g.-standard dye per l.)	Dyebath containing no added Na_2SO_4			Dyebath containing 0.0031 mol. Na_2SO_4 per l.			Dyebath containing 0.0155 mol. Na_2SO_4 per l.			Dyebath containing 0.031 mol. Na_2SO_4 per l.		
	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Dyebath / Fiber (C_B/C_F)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Dyebath / Fiber (C_B/C_F)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Dyebath / Fiber (C_B/C_F)	Fiber (milliequivalent per g.)	Dyebath (g.-equivalents per l.)	Dyebath / Fiber (C_B/C_F)
0.02	0.0021	0.07×10^{-4}	3.3×10^{-2}	—	—	—	—	—	—	—	—	—
0.1	0.0097	0.33×10^{-4}	3.4×10^{-3}	—	—	—	—	—	—	—	—	—
0.2	0.0200	0.64×10^{-4}	3.2×10^{-3}	—	—	—	—	—	—	—	—	—
0.4	0.041	1.31×10^{-4}	3.2×10^{-3}	—	—	—	—	—	—	—	—	—
0.5	—	—	—	0.043	2.30×10^{-4}	5.3×10^{-3}	0.031	3.5×10^{-4}	11.3×10^{-3}	0.027	3.9×10^{-4}	14.4×10^{-3}
0.75	—	—	—	0.067	3.22×10^{-4}	4.8×10^{-3}	0.048	5.1×10^{-4}	10.6×10^{-3}	—	—	—
1.0	0.100	3.09×10^{-4}	3.1×10^{-3}	0.089	4.28×10^{-4}	4.8×10^{-3}	0.066	6.6×10^{-4}	10.0×10^{-3}	0.058	7.4×10^{-4}	12.7×10^{-3}
1.5	—	—	—	0.136	6.2×10^{-4}	4.6×10^{-3}	0.101	9.7×10^{-4}	9.6×10^{-3}	—	—	—
2.0	0.184	7.55×10^{-4}	4.1×10^{-3}	0.178	8.6×10^{-4}	4.8×10^{-3}	0.130	13.3×10^{-4}	10.2×10^{-3}	0.119	14.5×10^{-4}	12.2×10^{-3}
2.5	—	—	—	0.222	10.7×10^{-4}	4.8×10^{-3}	0.168	16.1×10^{-4}	9.6×10^{-3}	—	—	—
3.0	—	—	—	0.257	13.8×10^{-4}	5.4×10^{-3}	0.191	20.4×10^{-4}	10.7×10^{-3}	0.171	22.4×10^{-4}	13.1×10^{-3}
3.5	—	—	—	0.292	16.8×10^{-4}	5.8×10^{-3}	0.224	23.7×10^{-4}	10.6×10^{-3}	—	—	—
4.0	—	—	—	0.316	21.1×10^{-4}	6.7×10^{-3}	0.292	28.4×10^{-4}	9.7×10^{-3}	0.216	31.0×10^{-4}	14.3×10^{-3}
5.0	—	—	—	0.369	28.9×10^{-4}	7.8×10^{-3}	0.280	37.8×10^{-4}	13.5×10^{-3}	0.253	40.5×10^{-4}	16.0×10^{-3}
6.0	—	—	—	0.380	40.9×10^{-4}	10.7×10^{-3}	0.336	45.4×10^{-4}	13.5×10^{-3}	0.274	51.5×10^{-4}	18.8×10^{-3}
7.0	—	—	—	—	—	—	—	—	—	0.309	61.0×10^{-4}	19.7×10^{-3}
8.0	—	—	—	0.404	64.5×10^{-4}	16.0×10^{-3}	—	—	—	0.300	75.0×10^{-4}	25.0×10^{-3}
9.0	—	—	—	—	—	—	—	—	—	0.330	85.5×10^{-4}	25.9×10^{-3}
10.0	—	—	—	0.442	87.0×10^{-4}	19.7×10^{-3}	—	—	—	0.311	101.0×10^{-4}	32.4×10^{-3}

* The dye has been assumed to act as a monobasic acid.

a nearly constant partition holds seems to increase. This cannot be explained by the use of equation (2), for the sulfate ion concentration tends to become more constant with increasing addition of sodium sulfate.

It is interesting to observe that the results obtained by Knecht[4] with Crystal Ponceau display a similar behavior when C_B/C_F is plotted against C_B. It is obvious that further investigation of greater precision is needed to clarify this anomalous behavior, and the information at present available does not justify much theoretical speculation as to causes, but it does at least indicate that the dyeing mechanism is more complex than has been supposed, and possibly that two separate mechanisms are involved.

SATURATION VALUES OF SOLWAY BLUE B ON DIFFERENT FIBERS

Since Solway Blue B is a typical level dyeing acid dye which probably depends mainly on the attraction of ionic groupings, saturation values for this dye should indicate the relative amount of basic groups in the different fibers. This is of special interest in the case of nylon and casein fiber, concerning which little is known, while wool and silk, the acid-combining capacities of which are well-known, should provide a check on the figures. The saturation values from the isotherms for the four fibers at pH 1.6 are given in Table VIII. The values at pH 1.35 have been ignored as there seems to be definite evidence of tendering at this acidity with nearly all the fibers, resulting in liberation of more amino-groups and a fictitiously high value for amino-groups in the fiber.

The values for wool and silk may be compared with values for the acid-combining power of these fibers determined

TABLE VIII

Saturation Values of Various Fibers with Solway Blue B at pH 1.6

Fiber	Saturation value (milliequivalent per g. of fiber)
Wool	0.72
Silk	0.18
Casein fiber	0.74
Nylon	0.06

by titration by various investigators. Most workers have found that wool absorbs about 0.8 milliequivalent of hydrochloric acid per g. of fiber. Thus, Speakman and Hirst[12] gave a value of 0.80 milliequivalent at pH 1.35, while Steinhardt and Harris[13,14] gave 0.77 milliequivalent at pH 1.47. Working with simple dye-acids, Goodall[5] found that wool absorbs up to 1.4 milliequivalents per g. With silk, Lloyd and Bidder[15] obtained a value of 0.17 milliequivalent at pH 1.6, while Gleysteen and Harris[16] gave 0.12 milliequivalent at pH 1.55, the acid used in both cases being hydrochloric acid.

The saturation values with Solway Blue B on wool and silk thus appear to be in reasonable agreement with these values, which lends support to the salt-linkage theory of dyeing with this particular dye. Data for titration of casein fiber with hydrochloric acid are not available, but from various published analyses of casein the maximum total amount of amino-groups is 2.26 milliequivalents per g. The difference between this figure and the saturation value with Solway Blue B is probably due to the process of hardening in which the casein fiber is treated with formaldehyde, which will block many of the amino-groups. The extreme similarity of the dyeing isotherms of casein fiber and wool is of considerable interest. At pH 1.6, the two curves are indistinguishable from one another. At pH 1.35 the casein fiber curve lies below that of wool, but it is doubtful whether much significance can be attached to this as both the wool and the casein fiber show signs of degradation. The close parallelism between the two fibers is rather surprising in view of their different dyeing behavior. Casein fiber dyes much more quickly than wool and, as a rule, dyes have poorer washing-fastness on the former fiber. Taken in conjunction with the present result, this seems to indicate that the main difference between casein fiber and wool lies in their physical properties rather than in chemical structure. The casein fiber is probably more porous, swells more rapidly in the dyebath and allows more rapid diffusion of dye in the fiber, i.e., gives a higher rate of dyeing and lower fastness properties. This is supported by the known swelling powers of casein fiber and wool, especially the gelatinization of the former in alkaline soap baths.

These results seem to indicate that in the past rather too much importance has been attached to the part played by chemical affinity in determining dyeing and fastness properties. The physical construction of the fiber can be as important, if not more important. The probable reason for this is that most dyeing processes, and certainly most fastness tests, are not equilibrium tests, but are carried out for a limited period of time, so that the rate factor in absorption or desorption becomes important. The rate factor will be particularly influenced by the compactness of the fiber structure.

The results obtained on nylon fiber are also interesting. All the evidence of the isotherms points to a behavior of nylon fiber which is similar to that of the other fibers, but with a much lower saturation value, and by inference the dyeing mechanism is probably similar. This is supported by experiments on desorption of

nylon yarn dyed with Solway Blue B with sulfate ions. The results indicate that a linear relationship holds between the concentration of sulfate in the dyebath and the amount of the dye removed from the fiber, more dye being desorbed as the amount of sulfate ions increases. This suggests that the reaction consists in combination of the dye or sulfate anions with cationic centers (probably from amino-groups) in the nylon fiber. The mechanism of nylon dyeing has already been discussed in greater detail in another paper from these laboratories.[37]

EFFECT OF pH AND OTHER DYES ON THE SATURATION VALUE OF WOOL

The saturation values of wool for the three dyes examined are summarized in Table IX. The combining capacity of wool for hydrochloric acid is about 0.82 milliequivalent per g. of fiber.

TABLE IX

	Dye (milliequivalent per g. of fiber)		
pH	Solway Blue B	Disulphine Blue V	Carbolan Blue B
1.2	—	1.32	2.10
1.35	0.94	—	—
1.6	0.72	—	—
1.7	—	—	1.61
2.2	—	0.88	0.86
6.1	—	0.18	0.29

All these dyes are dibasic, but their behavior in the dyeing process is unknown. The figures in Table IX are calculated on the assumption that both acid groups in the dye are combining with amino-groups in the fiber, and in the case of Solway Blue B it has been shown that this assumption leads to results which correspond to the known acid-combining capacity of wool. The slight excess absorption at pH 1.35 is undoubtedly due to partial hydrolysis of the wool with liberation of more basic groups. In the case of Disulphine Blue V the matter is complicated by the fact that the dye molecule also contains a quaternary ammonium group, and it is therefore possible for the dye to behave as a monobasic acid by internal salt formation. The fact that 1 g. wool can absorb 1.32 milliequivalents of this dye may therefore be explained in this way without the need for postulating additional attractive forces.

In the case of Carbolan Blue B, about two and a half times as much dye is absorbed as can combine with the amino-groups in wool. Even if it is assumed that here also the dye is behaving as a monobasic acid, which is less likely than in the case of Disulphine Blue V, this will not explain the high absorption of dye completely. This high absorption, however, takes place only at the very low pH value of 1.2 and there is some evidence of fiber damage at this high acidity. It was decided to determine whether hydrolysis of main peptide chains had occurred to an extent sufficient to account for this increased absorption. In this connection it is not sufficient merely to treat wool in a blank dyebath, for when a dyebath contains anions having a high affinity for wool, then the absorption of such ions by the wool will permit a freer entry of the oppositely charged hydrogen ions into the fiber. Consequently, the pH developed inside the fiber may be lower in the presence of dye than in its absence. Accordingly it was decided to dye wool with Carbolan Blue B at pH 1.2, then remove the dye and estimate the number of amino-groups. The following experiment was carried out.

Wool was dyed at 95° C. for 6 hr. in a 400 vol. liquor, adjusted with sulfuric acid to pH 1.35 and containing 7.5 g. of standard dye per l. The wool after this treatment was very fragile (see later) and easily fell to pieces. At the same time another sample of wool was treated under exactly similar conditions, but in absence of dye. The two samples, together with a fresh sample of untreated wool, were then desorbed separately by treatment overnight in a 25 per cent solution of pyridine. The wool was next washed with hot water, rinsed in cold 5 per cent sulfuric acid for 10 min. and then washed in running water for several hours. The three samples were dyed separately at pH 1.7 with Carbolan Blue BS at 95° C. for 6 hr. in 400 vol. of dyeliquor containing 7.5 g. of standard dye per l. The amount of pure dye absorbed by the three samples was—

	Milliequivalents per g. of fiber
Wool not previously dyed.....	1.72
Wool pretreated in blank dyebath	2.18
Wool previously dyed with Carbolan Blue B	2.16

There is thus evidence of considerable hydrolysis (not, however,[4] accentuated by the presence of dye), leading to the liberation of about 25 per cent more amino-groups. If it is assumed in addition that the dye is behaving as a monobasic dye, then the extent of hydrolysis is just about sufficient to account for the observed absorption of dye. In some cases Steinhardt and Harris[34] have observed abnormally high absorption with certain dibasic organic acids on wool and have attributed this behavior to the dibasic acid acting as a monobasic acid, each molecule combining with one ionized amino-group instead of two. As mentioned earlier, Goodall[5] has reported a similar excessive absorption of dye in the case of Polar Yellow R and Acid Orange GG, but in the case of the former dye the explanation of change in basicity cannot apply. In conclusion, therefore, it may be stated that with Carbolan Blue B there is definite evidence that wool will absorb about twice the amount of dye needed to saturate the amino-groups, but no evidence to support an absorption greater than corresponds with one dye molecule to each amino-group. Thus, it appears probable that the ionic mechanism is the governing factor in determining the extent of dye absorption and that any other forces which are involved merely assist in the fixation of the dye to the fiber, but cannot independently cause dye fixation on sites other than ionic sites.

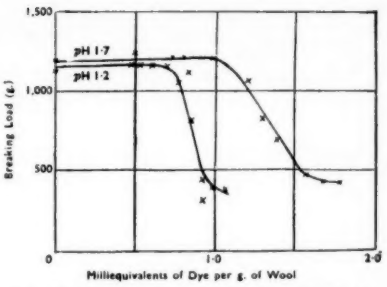


Fig. 10—Tendering of Wool with Carbolan Blue BS

DAMAGE TO WOOL BY HIGH CONCENTRATION OF DYE

In Goodall's experiments[5] it was observed that wool dyed heavily with Polar Yellow R became very fragile, and in the present experiments also, using Carbolan Blue BS at pH 1.2, it was noted that when a large quantity of dye was absorbed by the fiber it became so tender on drying that it could be powdered in the hand. Tensile strength measurements on yarn dyed with various quantities of dye indicated that the point at which tendering occurred was very critical at pH 1.2, but rather less so at pH 1.7, although the same effect was ultimately produced (see Fig. 10).

The critical point corresponds with the absorption of 0.82 milliequivalent of dye per g. of fiber at pH 1.2 and about 1.4 milliequivalents at pH 1.7. Astbury[38] has stated that wool dyed to saturation by the method of Porai-Koschitz is similarly tendered. This tendering cannot be attributed to hydrolysis of the peptide chains, since the extent is controlled by the amount of dye absorbed and since wool treated in a blank dyebath is not tender, although the experiments already described show that it is hydrolyzed to the same extent.

A possible explanation of this effect is that at high concentrations the dye absorbed by the fiber in its swollen condition forms small crystallites or aggregates inside the fiber pores so that, when the fiber is dried, it is mechanically disrupted by the presence of these particles. The existence of such dye aggregates in wool fibers has been detected by Astbury and Dawson[39] from X-ray observations and more recently by Royer and Maresh[20] from microscopical observation. In the present

experiments the wool was so deeply colored that microscopical examination revealed nothing. In view of the ease with which the dyed wool could be disintegrated, it was thought that it might provide a satisfactory subject for examination in the electron microscope and, accordingly, portions of the wool dyed heavily with Carbolan Blue BS were ground in a mortar with a very little dispersing agent and finally diluted with water to form a very fine stable dispersion, the particles of which showed Brownian movement in the microscope. A portion of this suspension was examined in the electron microscope, but the particles were neither found to possess any recognizable structure, nor could the crystallites of dye, if present, be differentiated from the wool. Support for this view of the tendering process is therefore lacking. It does, however, seem to be the most probable solution and hence this behavior will probably be associated only with dyes having large molecules. It should perhaps be emphasized that this tendering behavior was observed only with very high concentrations of dye on the fiber such as are never attained in practical dyeing; in normal depths of shade no tendering was observed.

SUMMARY

Isotherms for the absorption of three acid dyes of different types on wool, silk, casein fiber and nylon have been determined at several pH values. The results may be fitted by the Langmuir adsorption equation at high concentrations, but at low concentrations a departure from this equation is observed, from which it is inferred that the dyeing mechanism is more complex than simple salt formation. At high acidities, hydrolysis of wool occurs during dyeing, leading to increased dye absorption. The degree of hydrolysis is not increased in presence of dye. The amount of a typical colloidal dye absorbed is not in excess of the total number of basic groups present, provided that it is assumed that each amino-group in the fiber can combine with one dye molecule and not with one dye equivalent.

At very high concentrations of dye in the wool fiber, severe tendering takes place, which is attributed to mechanical disruption, due to the formation of large dye crystallites inside the water-swollen fiber, which cannot be accommodated on drying.

The absorption isotherms of wool and casein fiber are almost identical. Their chemical affinity for dye is thus the same, and the observed differences in rate of dyeing and wet fastness must be attributed to differences in physical structure. The dyeing mechanism with nylon appears to be similar to that of wool, and, from the quantity of crystalloidal dye absorbed, the fiber appears to contain 0.05 milliequivalent of basic groups per g., as compared with 0.2 milliequivalent per g. for silk and 0.7 milliequivalent per g. for wool and casein fiber.

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Wool-Acid-Water Relationships

(Concluded from Page 447)

(table 9). The revised curves are shown in figure 7.

Figure 8 shows the effect of the correction for non-volatile cationic ash on the wool-hydrochloric equilibrium curve.

Any attempt to adequately correct for more than this specific variable must await further, more complete data.

CORRELATION OF EMPIRICAL AND THEORETICAL DATA

It follows from a consideration of wool-acid-water relationships that there can be no strict agreement between the theoretical basic dissociation curve of wool and any empirical wool-acid combination curve. The wool dissociation curves are derived from mass law equations in which the H^+ added is hypothetically divorced from anions other than OH^-. Addition of an acid to manipulate the hydrogen-ion concentration introduces new variables. The acid itself dissociates according to the law of mass action, the presence of H^+ causes wool to dissociate as a base, and a combination of acid anion with basic wool groups occurs which can also be expressed quantitatively in terms of the mass law. The wool salt formation decreases the total number of basic wool groups, and changes the per cent dissociation of those remaining. This change in per cent dissociation is probably never in exact equilibrium with the changed $[H^+]$ of the bath except through coincidence. Further adjustments must take place to correct this condition of unbalance, and must continue until some state of mutually interdependent equilibrium is attained. This state of equilibrium is reached at a different point for each acid. One approach toward simpliyfying these complex interrelationships, and developing some sort of quantitative expression, is through individual mass law equations:

(1). *Water*

$$\frac{[H^+]\ [OH^-]}{[HOH]} = k_w$$

(2). *Acid*

$$\frac{[H^+]\ [A^-]}{[HA]} = k_a \text{ (different for each acid)}$$

(3). *Wool-basic dissociation*

$$\frac{[^+NH_3.W.COOH]\ [OH^-]}{[H_2O.NH_2.W.COOH]} = 'k_{wb}'$$

(4). *Wool-Acid Anion Salt*

$$\frac{[^+NH_3.W.COOH]\ [A^-]}{[A.NH.W.COOH]} = 'k_{ws}' \text{ (different for each salt)}$$

No attempt will be made to discuss this in a quantitative way until more data on wool-anion combination, particularly wool-large organic ion combination, have been presented.

TABLE 9
Corrections Applied to a Wool-Acid Equilibrium Curve for the Case in which the Isoelectric Point is at pH 5.0 and the Equivalence of the Cationic Ash is .052 Milli-Equivalents/Gram of Wool.

pH	*Corrections (milli-equiva-lents/gm.)*	pH	*Corrections (milli-equiva-lents/gm.)*
1.0	.0000	4.5	.035
2.0	.0004	4.75	.041
3.0	.004	5.0	.046
3.5	.013	5.5	.050
4.0	.021	6.0	.052
4.25	.028	>6.0	.052

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TRADE NOTES • NEW PRODUCTS

• MARSHAL WITH A.A.P.

Capt. James J. Marshal has returned to civilian life in the capacity of assistant to

James J. Marshal

the Executive Vice-president, G. L. Armour, of American Aniline Products, Inc. Capt. Marshal will make his headquarters at the New York office of the company.

• APPOINTED GLASGO MANAGER

In line with post-war plans, The Glasgo Finishing Company of Glasgo, Connecticut, has announced the appointment of Donald J. Eccleston as Assistant General Manager, and Arthur F. McLean as Superintendent and Technical Director.

Mr. Eccleston is a graduate of Brown University (Phi Beta Kappa). He was associated with The Glasgo Finishing Company for three years, and for the past five years he has been Service Manager for the Aridye Corporation.

Mr. McLean attended the University of New Hampshire and Lowell Textile Institute. He was associated with Pacific Mills for eight years as chemist, and with Cold Spring Bleachery for two years. For the past three years he was director of application laboratories for the Aridye Corporation.

• JOINS WARREN PRINT WORKS

Howard J. Revell has resigned after being Superintendent at The Glasgo Finishing Company for fifteen years to accept a position as Assistant General Manager with The Warren Print Works at Bondsville, Mass.

• SCHOLARSHIP AT LOWELL TEXTILE INSTITUTE

The drive of newly elected President Kenneth R. Fox of the Lowell Textile Institute for additional research scholarships, was given a boost by Joseph P. Kennedy, former ambassador to Great Britain, during his recent tour of Massachusetts, as chairman of Governor Tobin's special committee investigating State industries.

He presented a check for 1200 dollars to President Fox to found a yearly scholarship commemorating his son, the late Lt. Joseph P. Kennedy, Jr., USNR, who was killed piloting a Liberator bomber, August 2, 1944. The details of the scholarship are to be worked out later but it is designed for graduates of the Institute to enable them to do either industrial or advanced technical research for the benefit of the textile industry.

Mr. Kennedy and his State Commission spent a portion of their time inspecting the Institute and commented on the failure of Massachusett's industry to take a greater advantage of its outstanding research facilities. He put much of the blame for the decline in the number of industrial establishments in Massachusetts, to the unwillingness of industry to make adequate use of research as an aid to keeping abreast of the times.

The Institute has recently received several substantial donations for research scholarships and, as a result of President Fox's campaign, several more are expected to be announced soon. The increasing use of technical research in the textile industry makes research fellowships more and more important if the extensive testing and manufacturing equipment of the Institute is to be employed with a maximum advantage to industry.

• CALCO RELEASE

Calco has just announced the release of their Color Announcement Card on Calcosol Gray 2G Double Paste.

Calcosol Gray 2G Double Paste is a new anthraquinone vat dye for which patents have been applied for. It is claimed that this dyestuff has demonstrated exceptional fastness to light, chlorine and water spotting and in recent field trials has shown that it possesses outstanding level dyeing properties.

Because of high degree of dispersion, Calcosol Gray 2G Double Paste is of special interest for application by the pigment method of package dyeing and by the pad-jig method on cotton, viscose-rayon and linen piece goods.

Because of the fastness properties of Calcosol Gray 2G Double Paste, it is being recommended by the manufacturers for all types of cotton and viscose-rayon materials.

A copy of the new Calco Color Announcement may be obtained from your Calco representative or by addressing your request c/o Advertising Department, Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey.

• 40 YEARS WITH PHILADELPHIA QUARTZ

James G. Vail, Vice President and Director of the Philadelphia Quartz Company, Philadelphia, manufacturers of silicates of soda, recently celebrated 40 years of continuous service with the company. His fellow directors and associates tendered a testimonial luncheon in his honor at the Downtown Club in Philadelphia.

• "COOLNESS" TEST FOR FABRICS

The United States Testing Company, Inc. has been investigating methods of obtaining a measure of the relative coolness of fabrics for Summer wear.

A test method has been developed which classifies materials as to their "coolness" and suitability for Summer wear. The influence of such factors as moisture penetration, still and moving air, and exposure to various light illuminations, are taken into account in the measurements.

• TECHNICAL DIRECTOR, MORTON CHEMICAL

Morton Chemical Company, Greensboro, N. C., has appointed Dr. B. G. Zimmerman as Technical Director of the company. Dr. Zimmerman is now located at the laboratories and plant of the company at Greensboro and will supervise a considerable expansion in the research activities of the company.

B. G. Zimmerman

Dr. Zimmerman is a native of Shiner, Texas. He received his B.S. in Chemical Engineering from Texas A. & M., his M.S. in Chemical Engineering from the University of Texas, and his Ph.D. in Organic Chemistry from the University of

Texas. He has been employed for the past eight years in the Research Division of General Aniline Works, Grasselli, N. J.

Morton Chemical Company is just now completing work on the re-building and re-equipping of its plant following the fire of July, 1944. All presently contemplated facilities should be completed within about thirty days and the plant will then be equipped for the production of a wide range of organic specialties.

● AWARD FOR MATHIESON ANNUAL REPORT

The Mathieson Alkali Works has been awerded the *Financial World* citation and trophy—the "Oscar of Industry"—for the excellence of its 1944 Annual Report. Mathieson's report was selected as one of the two best stockholders' reports in the chemical industry. Awards were made for the two best reports in each of 50 business classifications, selected from a total of 2,500 entries. All were judged on the basis of financial, statistical and editorial content, format, typography and illustration.

The Mathieson report was judged a winner in the chemical classification by a board consisting of Dr. Lewis Haney, Professor of Economics at New York University; Norman Bel Geddes, industrial designer; C. Norman Stabler, Financial Editor of the *New York Herald-Tribune;* Glenn Griswold, former publisher of *Business Week* magazine; and Sylvia F. Porter, Financial Editor of the *New York Post.*

● APPOINTED MANAGER, STEIN-HALL, LTD.

Stein, Hall & Co., Inc., New York, has announced the resignation, effective January 1st, of A. R. McCleary as managing director of its Canadian affiliate, Stein-Hall, Ltd., Toronto, Ontario, and the appointment of David McGill as general manager, with E. F. Clark as assistant manager.

Mr. McCleary has been connected with Stein-Hall, Ltd. since its inception. Mr. Clark has been Purchasing Agent and Production Manager for ten years.

Stein-Hall & Co., Inc. and its Canadian affiliate manufacture and distribute starches, gums, dextrines, liquid and dry adhesives and other raw materials and specialty products used by many industries, and import burlap and other commodities.

Mr. McGill joined the Canadian Active Army in August 1943 and has been attached to the Army Technical Development Board at Canadian National Defense Headquarters in Ottawa. He completed his Army service as a Major recently and joined Stein-Hall on October 15th.

● JOINS CALCO

The Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey, announces that Dr. Victor E. Wellman will join the staff of its Development Department, on January 1,

Victor E. Wellman

1946. In addition to his development work, Dr. Wellman will serve as Technical Advisor to the Sales Department on matters relating to Intermediates and Chemicals. He is presently connected with R. W. Greeff & Company, Inc., New York, and was for 15 years with the B. F. Goodrich Company, Akron, Ohio.

● DCAT SECTION MEMBERSHIP

"The Drug, Chemical and Allied Trades Section of the New York Board of Trade has achieved a new 'high' in membership, with 600 of the most representative firms in the drug, chemical and allied industries now listed on its roster," announced Lloyd I. Volckening, Chairman of the Section's Membership Commitee (and President of The Ivers-Lee Company).

Indicating that 80 of these companies had become affiliated with the Section within the past few months, Mr. Volckening added—"Mere numbers alone are not significant. One of the prime factors in the steady expansion and development of the Section is the consciousness on the part of firms in the drug, chemical, cosmetic and allied trades that the DCAT Section contains within its membership representation from every branch of the industry and from every part of the country, all having an equal voice in formulating the policies of the association."

● REJOINS ARNOLD, HOFFMAN

Arnold, Hoffman & Co., Inc., manufacturing chemists with main offices in Providence, R. I., announces that Captain W. Chester Cobb has rejoined their staff as Southern Sales Manager, effective October 1, 1945. Captain Cobb will make his headquarters at the Charlotte, North Carolina office of the Company,—2130 North Tryon Street,—and will have general sales supervision of all territory south of Washington, D. C.

Captain Cobb has recently completed distinguished service with the United States Army overseas.

● HONORARY MEMBERS, COTTON MANUFACTURERS ASSOCIATION

At the Annual Meeting of the National Association of Cotton Manufacturers, Edward W. France, former Director of the Philadelphia Textile School and a member of the Association since 1896, and Charles H. Eames, former President of the Lowell Textile Institute and a member of the Association since 1907, were unanimously elected Honorary Members of the Association, in recognition of their outstanding contributions to the industry through raising the standards of textile education.

● FRARY TO GET PERKIN MEDAL

Dr. Francis C. Frary, Director of Research of Aluminum Company of America, has been elected to receive the Perkin Medal in recognition of his outstanding accomplishments in the field of industrial research, it was announced recently by Cyril S. Kimball, Secretary of the American Section of the Society of Chemical Industry. The presentation of the medal will take place at a dinner meeting of the society at the Hotel Commodore on the evening of January 11, 1946.

Dr. Frary is the fortieth member of a group of distinguished scientists to receive the Perkin Medal. He is also the second scientist on the staff of Aluminum Company of America to be so honored. In 1911, Charles Martin Hall was awarded this coveted medal for his development of the present day process for the manufacture of aluminum.

● DU PONT APPOINTMENT

The Du Pont Company announced that, effective Oct. 15, Dr. John M. Clark, assistant production superintendent of the Chambers Works, Deepwater, N. J., was appointed to the newly created position of general superintendent of the Photo Products Department with headquarters at Wilmington.

● ANNUAL MEETING, C.T.I.

The Cotton-Textile Institute announces that it has postponed its annual meeting, originally scheduled for October 24-25 to November 28-29. The sessions will be held at the Waldorf-Astoria Hotel, New York City.

● NEW DU PONT OFFICE BUILDING

Plans for a new 18-story office building to be erected at Tenth and Tatnall Streets

in Wilmington as an addition to the Nemours Building have been announced by E. I. du Pont de Nemours and Company.

Construction is to start next Spring, and the new structure will be completed by the Spring of 1947. A preliminary estimate of the cost is approximately $3,000,000.

The building will be 230 feet in height and will occupy the plot on which the present Nemours Building Annex stands, having a net ground area of 15,600 square feet with fronts of 71 feet on Tatnall Street and 121 feet on Tenth Street. The Annex, formerly the Wilmington Auto Company building, will be razed to make way for the new project.

• RESIDENT MANAGER, WOOD WORSTED

Ending a career of more than 30 years in the Army, Colonel Vere Painter, officer in charge, Headquarters, Inspection Service, Army-Navy Purchasing Office, 111 East 16th Street, New York City, left recently on terminal leave, pending his retirement. He will become resident manager of the Wood Worsted Mill, American Woolen Co., Lawrence, Mass. Colonel Painter has served with the Quartermaster Corps since 1920, and prior to that was in the Infantry.

• BOOKLET ON CELLULOSE ACETATE

A revised edition of the technical reference booklet on cellulose acetate has just been issued by Hercules Powder Company. This brings up-to-date the fundamental literature on the three major bases for cellulosic plastics. Revisions of the ethyl cellulose and nitrocellulose booklets were issued several months ago and are still available.

Included in the plastics material of the revised cellulose acetate booklet is a new section on the use of cellulose acetate in thermoplastic laminates. The improved dimensional stability and greater water resistance of plastics made from high acetyl acetate is also discussed in the booklet.

In addition to the information on plastics, the booklet suggests many other uses of Hercules cellulose acetate in rayon, film and foil, and specialty lacquers.

• A.S.T.M. STANDARDS ON SOAPS AND OTHER DETERGENTS

A.S.T.M. has again issued its special compilation of specifications and tests on Soaps and Other Detergents (with Related Information). The 29 specifications and tests covered are a result of intensive work carried out by Committee D-12 on Soaps and Other Detergents.

The specifications for soap cover bar, chip, powdered, salt water, solid, toilet, etc. Specifications for detergents cover soda ash, caustic soda, modified (sesquicarbonate type), sodium sesquisilicate, trisodium phosphate and tetrasodium pyrophosphate. Methods of test include sampling and chemical analysis of soaps and soap products, soap containing synthetic detergents, special detergents, sulfonated and sulfated oils, metal cleaning compositions (industrial), etc. Definitions of terms applying to these materials are given.

An extensive 30-page bibliography of aluminum and other metal cleaning is included.

Copies of the publication in heavy paper cover can be obtained from A.S.T.M. Headquarters, 260 S. Broad Street, Philadelphia 2, Pa., at $1.75 per copy.

• NORTHERN SALES MANAGER, ARNOLD, HOFFMAN

Arnold, Hoffman & Co., Inc., manufacturing chemists wtih main offices in Providence, Rhode Island, announces the appointment of Leonard G. Tubbs as Northern Sales Manager, effective October 1, 1945.

Mr. Tubbs will make his headquarters in the New York office of the company at 350 Fifth Avenue, where he has been located for some years. He will have general sales supervision of all territory north of Washington, D. C.

• SONNEBORN WOOL LUBRICANT

A new self-scouring wool fiber lubricant, which is said to possess remarkable wetting and detergent properties, and to offer important advantages over conventional self-emulsifying oils, has been announced by the Textile Chemicals Division of L. Sonneborn Sons, Inc., 88 Lexington Ave., New York 16. Outstanding features of the new product, known as Fybrol 1115 (patent pending), are said to be its complete self-scourability and its inherent ability to form a stable, opalescent solution (not an emulsion) which is soluble in hot water, oil and petroleum solvents and does not break at room temperatures or when diluted with cold water.

Among other advantages claimed for Fybrol 1115, a sulfonated hydrocarbon whose characteristics are adaptable to all phases of wool processing, are the following: Uniform distribution of the oil on the fiber throughout the various processing steps; utilization of residual Fybrol 1115 for soapless fulling by the addition of a small amount of soda ash; ultimate removal of the oil by a simple water rinse.

It is stated that Fybrol 1115 can be utilized to excellent advantage in wet finishing such as fulling, scouring and dyeing. It is further said to remain unaffected in low concentrations of acid, alkali and salt, a feature of special importance in piece carbonizing, acid or alkali fulling.

Representing a new and radical departure from previously accepted methods of wool-fiber lubrication, Fybrol 1115 is the result of many months of intensive work in the Sonneborn textile research laboratories. Following rigorous tests in the company's laboratories, the new product was subjected to trial mill runs in a number of wool processing plants using various types and grades of virgin, Australian and reworked wool as well as mohair.

The results of these mill tests, the manufacturer stated, provided convincing proof of the overall superiority of Fybrol 1115 in the processing of wool yarn for blankets, fine suitings, coating fabrics, high quality felts, knitted and other wool fabrics, on the following points: (1) lower processing costs; (2) finer yarns of improved tensile strength; (3) softer, loftier finished fabrics with good coverage; (4) increased loom efficiency; (5) no discoloring of yarn or development of odor, and (6) cleaner cards.

A copy of a folder describing Fybrol 1115 may be obtained on request.

• NEW FINISHES AT DAN RIVER MILLS

New finishes for cotton roving and yarns treated with various synthetic resins and other bonding agents, have just been announced by the Research Engineering Division of Dan River Mills.

It is stated that improved physical construction of these yarns, and their application to a greatly broadened field of commercial uses, has also marked the year that has elapsed since these revolutionary processes first emerged from Dan River laboratories.

Progress has been steady in the improvement of the machines by which roving and yarn are treated with bonding agents, so that today the productivity of such machines is said to be much greater than a year ago.

Particularly encouraging results have been obtained in polished yarn by new processes which are said to eliminate some of the costly operations heretofore necessary in the conventional methods of polishing yarns.

A polished yarn of natural color, 3 ply 6s, produced by this new process is said to show high tensile strength, great evenness and smoothness and a generally fine appearance. The polishing is accomplished simultaneously with the curing of the synthetic resin bonding agent. The character of this yarn and the economical manner of its production are said to in-

dicate its adaptability to many of the uses for which polished yarns are required.

It is claimed that these improvements have all been gained without affecting the increased tensile strength, better stretch control and other factors that gave these products recognition as actually new articles of textile manufacture.

The great interest shown by the world textile industry in these developments has been evidenced by the large number of mill executives and technologists who have visited Danville in the past year. Working arrangements have been made on an international scale with textile men who are cooperating with the Dan River research staff in further development of the various synthetic resin processes.

In line with its policy of disclosing to the industry informative data on new yarn finishes and application, the Dan River research staff has summarized these developments as follows:

Belting cord, particularly suitable for automotive fan belts, said to show greatly increased strength and very considerable gains in running time of such belts in actual use.

Yarns especially treated for use in weaving spinning tapes; such spinning tapes are said to have much higher tensile strength and resistance to abrasion, better control of stretch and less tendency to slipping; grease and oil repellent.

Fiber Bonded roving especially adapted to braiding high-strength rope; mildew proofed in the same bath.

Sewing thread treated and dyed in the same operation and said to have high tensile strength and flexibility with controlled stretch.

Sewing thread especially treated for the sewing of shoe soles; claimed to show higher breaking strength than the same thread made of expensive cotton; adapted to the absorption of wax and other lubricants in the sewing process; also suitable for luggage and harness sewing.

Roving and ply yarn treated with a bonding agent of an entirely new type, said to have high tensile strength and exhibiting a very even, smooth and glossy finish, highly adaptable to weaving; also said to show a consistent and fairly rapid recovery of stretch, thus fulfilling the requirements of those specialized types of yarns, known as "yarns with a memory."

Especially adapted florists' twine, a Fiber Bonded and dyed yarn of high strength and flexibility.

Low-grade cotton roving made from waste, rough and uneven, is said to be converted by Fiber Bonded treatment into cord of greater evenness and showing an increase from an original breaking strength of 7 pounds to a final breaking strength of 14 pounds.

All-purpose Fiber Bonded twine products, suitable for many uses: said to be tough and resistant to abrasion; this twine may be dyed in any color in same resin treatment bath.

High tensile strength 3 ply 6s yarn, glazed, dyed and bonded in one bath, thus reducing cost; suitable for multiform uses as twine.

Fiber Bonded roving encased in heavy resin coating; may be dyed in the same resin bath; said to have high tensile strength and to be adaptable to various coated-yarn uses.

Variations in rovings treated with bonding agents; in natural finishes and in colors; highly flexible or very stiff and wiry; and illustrative of the wide range of characteristics which may be imparted to a Fiber Bonded roving or to a yarn by these new chemical treatments.

• JOIN APEX CHEMICAL

Stanford L. Hermann, Operating Vice President of the Apex Chemical Company, 200 South First Street, Elizabeth, N. J., has approved the appointments of the following personnel to the staff of the Research Laboratories:

Arthur Regan, Chemical Engineer, graduate of the Newark College of Engineering, where he was previously employed as Assistant to Dr. James Bradley. Under Dr. Bradley he did research on various emulsifying agents. At Apex, Mr. Regan has been made assistant to the Production Manager, Charles L. Coble.

A. Seldner, graduate of Columbia University in 1940 with Phi Beta Kappa honors. His previous work, experience with the Trubek Laboratories and the Ciba Pharmaceutical Company has resulted in his appointment to the organic chemical staff headed by Dr. Philip Levine. In this capacity, he will be responsible for the promulgation of organicals which the Apex Chemical Company is at this time making, as the results of the purchase of the entire facilities of the K & S Chemical Company, 44 Cliff Street, New York City.

• COURSE ON HOSIERY AND KNIT GOODS

In response to a demand for more adequate training in hosiery and knit goods manufacture, the School of Textiles at N. C. State College has adopted a series of new courses organized in the form of a curriculum which enables students to specialize in this important branch of the textile industry, it was announced recently by Dean Malcolm E. Campbell, head of State College's School of Textiles.

The new courses, Dean Campbell said, are framed around the established methods of knit fabric structure and the fabrication of garments and knitted novelties. The importance of management training also is recognized, and a liberal allotment of credits has been provided for instruction in industrial and personnel management and mill organization, including time study methods, rate settings, cost methods, economics, and accounting.

Provision also is made for training in business psychology, natural and synthetic fiber studies, and language, Dean Campbell explained.

Additional information may be secured by writing to Prof. W. E. Shinn, head of the knitting department in the State College School of Textiles.

From the REPORTER FILES

TEN YEARS AGO

THE Nominating Committee of the A.A.T.C.C. presented the following slate: President—William H. Cady; Vice-Presidents—Elmer C. Bertolet and Arthur R. Thompson, Jr.; Treasurer—William R. Moorhouse; Secretary—Harold C. Chapin; Councilors-at-large—Harold M. Chase and Arthur E. Hirst. . . . The initial meeting of the Rhode Island Chapter of the Lowell Textile Institute Alumni Association was held on September 12th in Providence. . . . More than 300 students were enrolled at the Textile School of North Carolina State College. . . A combined business meeting and outing of the Sulfonated Oil Manufacturers' Association was held on September 20th at the Manufacturers' Country Club near Philadelphia. . . .

TWENTY YEARS AGO

DANIEL KNOWLAND, secretary of the New York Section of the A.A.T.C.C., reported that Henry Herrmann presented a paper entitled "Further Notes on the Science of Dyeing" at their September 25th meeting at the Machinery Club. There were forty-two present for dinner and a total attendance of sixty. . . . More than 500 persons attended the Fourth Annual Chemical Industries Dinner at the Hotel Roosevelt, New York, on October 1st.

TWENTY-FIVE YEARS AGO

GEORGE H. ASHTON, New Haven manager of S. R. David & Co., Inc., was elected a director of the company. . . . The report by E. S. Chapin to the Dye Advisory Committee of the State Department was published in the October 11th issue. Mr. Chapin was Paris representative of the Textile Alliance, Inc. . . . Sandoz Chemical Works, Inc., announced that the selling force of the dyestuff business of F. Bredt & Co. was united with theirs. . . Charles E. Bagley was appointed Northeastern manager of the dye and chemical department of the Sherwin-Williams Co. . . .